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SECTION-A

PART IV

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**Determination of carbosulfan and propoxur in environmental samples employing p-amino-acetanilide**

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**Abstract**

A simple, rapid, sensitive and accurate spectrophotometric method is developed for the determination of carbosulfan and propoxur in field water samples and grains. The method is based on the formation of coloured species upon coupling their hydrolysis products with diazotized p-aminoacetanilide, exhibiting maximum absorption at 390 and 389 nm respectively. The method obeys Beer's law over the concentration range 0.5 - 12 and 0.5 - 16 µg/ml.

**(Keywords.** spectrophotometry/carbosulfan, propoxur determination / p-amino-acetanilide / chloroform)

**Introduction**

Carbosulfan, carbamic acid [(dibutylamino)thio]methyl-2,3-dihydro-2,2-dimethyl-7-benzofuranyl ester is a recently developed broad spectrum systemic and contact insecticide belongs to the class of carbamate insecticides. It is used for the control of soil dwelling insects and foliar pests on maize, potatoes and sugarbeet and also used as a nematicide. It acts as a cholinesterase inhibitor. Carbosulfan is unstable in acid

medium and it will be converted into carbofuran by N-S bond cleavage. Clay *et al*<sup>1</sup>, have reported the activity of this compound

Propoxur, 2-(1-methyl ethoxy) phenyl methyl carbamate also belongs to carbamate class of pesticides. It is a white crystalline solid having m.p. 91°C, soluble in most organic solvents. Propoxur is commercially available as 1% Baygon spray, 2% bait, 4% Baygon and 70% wettable powder. Baygon has rapid knockdown and long residual action. It shows cholinesterase inhibiting properties and is particularly effective as an insecticide. It is particularly effective against insects affecting man and animals, such as cockroaches, flies and mosquitoes. Foilage sprays have given effective control of aphids, lygus bugs, grass hoppers and other insects on various crops. Bioactivity and persistence of propoxur in mineral soil, river water and in the aquatic environment have been reported<sup>2-4</sup>. Wide spread application of these carbamate pesticides to control pests in agricultural as well as domestic applications. All these pesticides from the agricultural field, and domestic applications are washed over the nearby water sources either by leaching or by the surface runoff. Such residue concentration are more than the permissible levels and are generally harmful to pond fauna and the people who drink these waters.

Literature survey revealed that very few analytical methods such as GC<sup>5-6</sup>, HPLC<sup>7-11</sup> and TLC<sup>12-15</sup> and some other spectrophotometric methods<sup>16-23</sup> have already been reported. The present communication reports a new spectrophotometric method for the determination of the above pesticides based on the formation of a coloured species by coupling the corresponding phenols obtained by alkaline hydrolysis with diazotized p-aminocetanilide.

### Materials and Method

All chemicals used were of analytical grade and all of the solutions were freshly prepared with distilled water. A Hitachi, model U-3400, UV-VIS NIR Spectrophotometer with 1 cm glass cells was used for absorbance measurement. Sodiumhydroxide (2%) and sodiumnitrite (0.5%) solutions were freshly prepared. p-aminoacetanilide solution (0.1%) is prepared in 100ml 1N hydrochloric acid.

#### *Preparation of standard solutions of Carbosulfan and Propoxur (50 µg/ml) :*

Stock solution of the above pesticides were prepared by dissolving 50 mg of analytical grade insecticide in 100ml of methanol. From this working standard solution is prepared by diluting 10 ml of this solution to 100ml.

*Preparation of sample solution .*

Formulations: Carbosulfan 25% and Propoxur 70% wettable powder. An amount equivalent to 50 mg of the insecticide was dissolved in 50 ml of methanol. 5 ml aliquots of the solution was subsequently diluted with 100ml of methanol.

*General Procedure :*

Aliquots of standard insecticide solution (50 $\mu$ g/ml) 0, 0.25, 0.5, 1.0, . . . . ., 6ml were placed in series of 25 ml standard flasks followed by adding 2.5ml of 2% sodiumhydroxide and 2.4ml of diazotization mixture. The solutions were made to the mark with distilled water and absorbance was measured for the yellow coloured chromophore against a reagent blank. The absorbance is plotted against the final concentration to obtain a calibration graph.

*Water samples* : pH of each water sample was adjusted to 3-4 with 20% sulphuric acid. One litre samples of distilled water and tap water was fortified with different concentrations of insecticide dissolved in methanol. The fortified water samples were extracted with 100ml chloroform using a separating funnel. Chloroform extracts were collected into a funnel and re-extracted the aqueous phase twice with 50ml chloroform. The combined extracts were washed with 0.1 M potassium carbonate solution and dried over anhydrous sodium sulphate in a filter funnel and collected the extracts in a 250ml standard flask. Finally these were made upto the mark with chloroform. Known aliquots of the chloroform were evaporated to dryness on a steam bath. The residue was dissolved in methanol, then developed the colour.

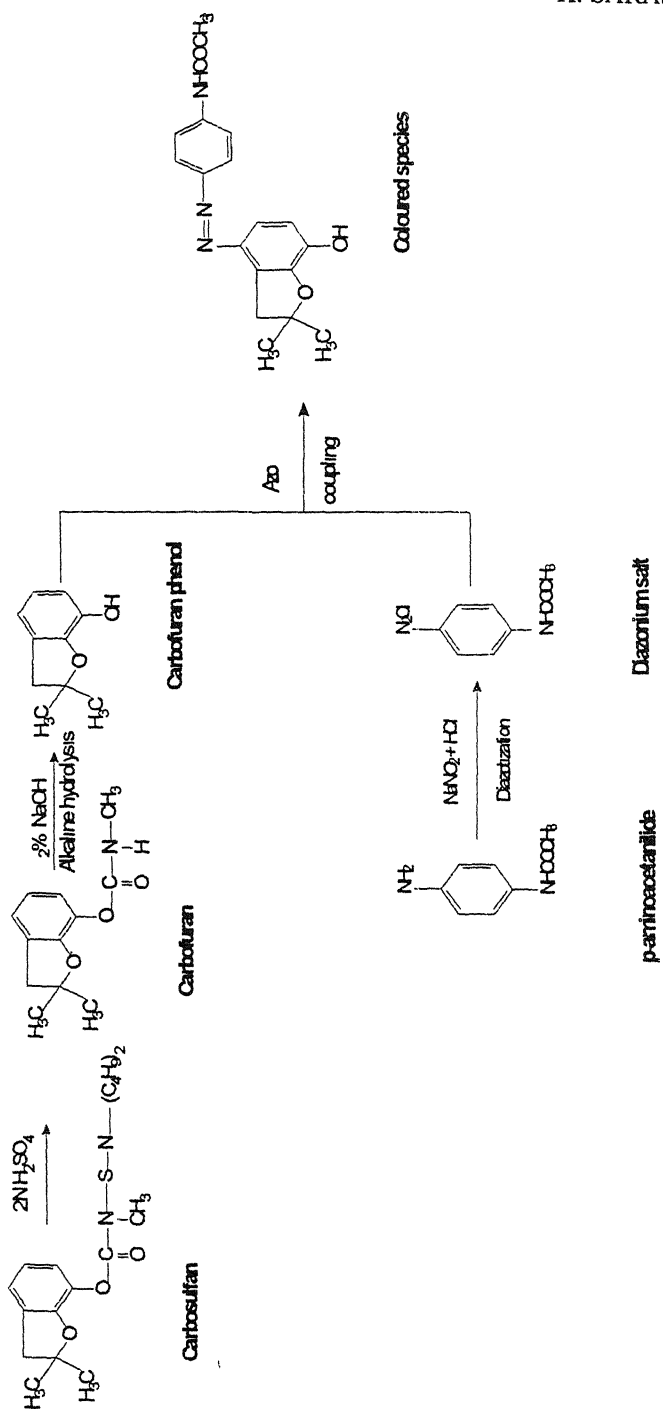
*Grains* : 100g of grains (rice and wheat) was taken in a conical flask and shaken for 5 min, with 200ml chloroform. Chloroform was filtered into a 250ml standard flask through a Whatman No.1 filter paper and residue was washed twice with 10ml chloroform. Chloroform extracts were combined and made up to the mark. Known aliquots of the chloroform extracts were used for colour development after evaporating chloroform.

### Results and Discussion

The absorbance maximum was at 390nm for Carbosulfan and 389nm for Propoxur. Beer's law is obeyed over the range 0.5-12  $\mu$ g/ml for Carbosulfan and 0.5-16  $\mu$ g/ml for Propoxur. The colour develops instantaneously and remains stable for more than 24 h. The coupling reaction can be done at room temperature only.

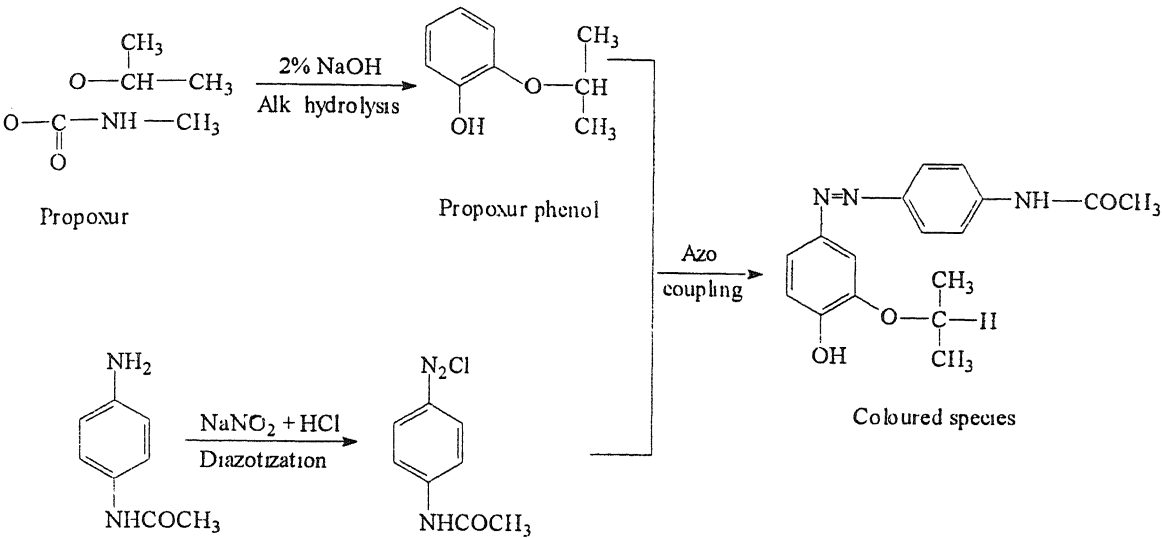
The suitability of the proposed method was studied by analysis of ten replicate samples containing 5ppm of Carbosulfan and Propoxur. The relative error and relative standard deviations are given in Table 1.

## Reaction Mechanism



Carbosulfan with p-aminoacetanilide

Reaction Mechanism



p-aminoacetanilide

Propoxur with p-aminoacetanilide

Table 1– Characteristics of the method

| Parameter   | Carbosulfan         |                                | Propoxur            |                                |
|---|---------------------|--------------------------------|---------------------|--------------------------------|
|   | Present work        | Reference method <sup>19</sup> | Present work        | Reference method <sup>18</sup> |
| $\lambda_{\text{max}}$ , nm                                 | 390                 | 475                            | 389                 | 500                            |
| Beer's law limit, $\mu\text{g/ml}$                          | 0.5-12              | 1-10                           | 0.5-16              | 0.25-5.0                       |
| Sandell's sensitivity, $\mu\text{g cm}^{-2}$                | 0.0083              | -                              | 0.0125              | -                              |
| Molar absorptivity, $\text{litre mole}^{-1} \text{cm}^{-1}$ | $4.576 \times 10^4$ | -                              | $1.674 \times 10^4$ | -                              |
| Stability of the coloured species, hr                       | 24                  | 8                              | 24                  | 12                             |
| Relative Standard Deviation, %                              | 0.91                | 0.8                            | 0.4                 | 0.6                            |
| Relative Error, %   | 0.5                 | 0.6                            | 0.2                 | 0.3                            |

Formulations containing Carbosulfan and Propoxur were analysed (10 replicates). For a 25% Carbosulfan emulsion the mean  $\pm$  standard deviation was  $24.48 \pm 0.12\%$ . For a 1% Propoxur spray and 4% dust the corresponding values were  $0.96 \pm 0.08\%$  and  $3.84 \pm 0.02\%$  respectively.

Recovery experiments were performed with known amounts of the compounds added to different samples of grains and water. For water samples a methanol solution of the insecticides was added. Grain samples were spiked by adding a methanol solution of the insecticide to the dry grains and evaporating the solvent.

The results presented in Table 2 show that recovery was in the range 95 to 97%. The results in Table 3 suggest that the method is applicable to the analysis of field water samples also.

Table 2— Recovery of Carbosulfan and Propoxur from grains and spiked water samples.

| Sample | Carbosulfan |                   |                                | Propoxur    |                 |                                |
|--------|-------------|-------------------|--------------------------------|-------------|-----------------|--------------------------------|
|        | Recovery, % |                   |                                | Recovery, % |                 |                                |
|        | Added, ppm  | Present work      | Reference method <sup>19</sup> | Added, ppm  | Present work    | Reference method <sup>18</sup> |
| Rice   | 1.0         | $96.4 \pm 1.9\%$  | $96.0 \pm 1.6$                 | 1.0         | $96.5 \pm 1.6$  | $96.0 \pm 1.2$                 |
|        | 3.0         | $96.2 \pm 1.0\%$  | $96.0 \pm 1.2$                 | 3.0         | $96.25 \pm 1.0$ | $96.0 \pm 1.0$                 |
|        | 5.0         | $95.4 \pm 0.9\%$  | $94.8 \pm 0.8$                 | 5.0         | $96.17 \pm 0.8$ | $95.8 \pm 0.8$                 |
|        | 7.0         | $94.8 \pm 0.7\%$  | $93.5 \pm 0.6$                 | 7.0         | $95.38 \pm 0.6$ | $94.7 \pm 0.6$                 |
| Wheat  | 1.0         | $96.40 \pm 1.2\%$ | $95.0 \pm 1.4$                 | 1.0         | $97.0 \pm 1.4$  | $96.0 \pm 1.4$                 |
|        | 3.0         | $96.20 \pm 1.0\%$ | $94.1 \pm 1.0$                 | 3.0         | $96.50 \pm 0.9$ | $95.6 \pm 1.0$                 |
|        | 5.0         | $95.17 \pm 0.8\%$ | $93.2 \pm 0.7$                 | 5.0         | $96.33 \pm 0.5$ | $94.7 \pm 0.9$                 |
|        | 7.0         | $95.00 \pm 0.6\%$ | $92.8 \pm 0.5$                 | 7.0         | $95.63 \pm 0.4$ | $93.0 \pm 0.7$                 |
| Water  | 1.0         | $96.20 \pm 1.0\%$ | $96.0 \pm 1.6$                 | 1.0         | $97.5 \pm 1.2$  | $97.2 \pm 1.0$                 |
|        | 3.0         | $96.75 \pm 1.0\%$ | $96.0 \pm 1.2$                 | 3.0         | $97.75 \pm 0.9$ | $97.0 \pm 1.0$                 |
|        | 5.0         | $96.0 \pm 0.9\%$  | $95.2 \pm 0.8$                 | 5.0         | $96.5 \pm 0.7$  | $96.3 \pm 0.9$                 |
|        | 7.0         | $95.60 \pm 0.7\%$ | $94.6 \pm 0.7$                 | 7.0         | $95.5 \pm 0.6$  | $95.1 \pm 0.7$                 |

Table 3— Determination of Carbosulfan and Propoxur in field water samples

| Sample Volume, ml | Carbosulfan found, ppm |                                | Propoxur found, ppm |                                |
|-------------------|------------------------|--------------------------------|---------------------|--------------------------------|
|                   | Present work           | Reference method <sup>19</sup> | Present work        | Reference method <sup>18</sup> |
| 250               | 0.20                   | 0.20                           | 0.18                | 0.14                           |
| 250               | 0.30                   | 0.29                           | 0.28                | 0.26                           |

The results obtained by the proposed method are found to be superior to the reference methods<sup>18-19</sup>. The method can be compared favourably with the reported methods<sup>18-19</sup>. As of its favourable characteristics as regards its stability, sensitivity and selectivity, the method can find applications to the field water samples also.

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### References

1. Clay, V E., Fahmy, M A H, Martin, J P & Fukuto, T T (1980) *J Agric Food Chem* **28** . 1122.
2. Read, D C (1971) *J Econ Entomol* **64** 800.
3. Eichelberger, J W. & Litchenberg, J (1971) *J Envi Sci Techol* **5** 541
4. Aly, O M & El-Dib, M A. (1971) *Water Res* **5** 1191
5. Moye, H A. (1975) *J Agric Food Chem* **23** 415
6. Sakave, S (1987) *Agric Biol. Chem* **51** 1239
7. Jansen, H, Brinknen, U.A.T & Frer, R W. (1985) *Chromatogr* **20** 453.
8. Engelhardt, H. & Lillig, B (1986) *ibid* **21** · 136.
9. Nunes, G.S, Riberio, M L, Polese, L. & Barcelo, D. (1998) *J Chromatogr* **795** (1) 43
10. Abad, A., Moreno, M J, Pelegri, R, Martinez, M I, Saez, A Gamon, M & Montoye, A. (1999) *J Chromatogr* **833** (1) · 3.
11. Carabia-Martinez, R, Rodriguez-Gonzalo, E, Paniagua-Macros, P H & Hernandez-Mendez, J (2000) *J Chromatogr* **869** (1-2) 427

- 12 Sevalker, M T , Patil, V B & Garad, M V (2000) *J Planar Chromatogr Modern-TLC* **13** (3) 235
13. Ambrus, H , Hargitai, E , Karoly, G , Fulop, A & Lantos, J (1981) *J Assoc Offi Anal Chem* , **64** 743
- 14 Appaiah, K.M., Nag, U C , Puranark, J , Nagaraja, V & Kapur, O P (1984) *Indian Food Packer*, **38** 28
- 15 Bracha, J (1964) *J Agric Food Chem* **12** . 461
- 16 Ramaswamy, M (1974) *Pestic Sci* **5** 383.
- 17 Mukherjee, G , Mukherjee, A K & Roy, B R (1975) *J Food Sci Tech* **12** 96
- 18 Appaiah, K.M , Kapur, O P & Nagaraja, K V (1983) *J Assoc Off Anal Chem* **66** 105
19. Rajeswari, C V & Naidu, P R (1986) *J Food Sci Tech* **23** 101
- 20 Naidu, D V & Naidu, P R (1990) *Talanta* **37** 629
- 21 Venkateswarlu, P , Kumar, V C & Seshiah, K (1995) *Indian J Chem* **34** 67
- 22 Delaguardia, M., Khalaf, K D , Carbonell, V & Moralesrubin, A (1995) *Anal Chim Acta* **308** 462.
23. Raju, J , Shrivhare, P. & Gupta, V K (1997) *International J Environ Anal Chem* **49** 111

## Synthesis and characterization of Mn(III), Fe(III), Zr(IV), Th(IV), VO(II) and UO<sub>2</sub>(II) chelates with 4,4'-dihydroxy-3,3'-dipropylbiphenyl-*o*-phenylenediamine

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### Abstract

4,4'-Dihydroxy-3,3'-dipropylbiphenyl-*o*-phenylenediamine (DDPBPD) and its chelates with Mn(III), Fe(III), Zr(IV), Th(IV), VO(II) and UO<sub>2</sub>(II) have been synthesised. These chelates have been characterized on the basis of elemental analysis, magnetic susceptibility, IR, electronic spectra and TGA analysis. The I.R. spectral studies indicate that the ligand acts as a dibasic tetradentate and coordinates through phenolic OH and azomethine nitrogen. The dependence of the electrical conductivity on the temperature has been studied over the temperature range 300-520 K and the chelates are found to show semiconducting behaviour. Thermogravimetric studies indicate the presence of water molecules in the Fe(III), Zr(IV) and Th(IV) chelates.

(**Keywords** IR/electronic spectra/polyschiff base/polychelates/TGA/electrical conductivity)

### Introduction

Polymeric co-ordinating reagents are a novel type of substance possessing a combine action of the physical properties of high polymer and the chemical properties of the attached reagents<sup>1</sup>. The facile regenerability, higher stability and operational flexibility of the co-ordination polymers have created considerable research interest in the recent years<sup>2</sup>. The present paper describes the synthesis and characterization of chelates derived from 4,4'-dihydroxy-3,3'-dipropylbiphenyl-*o*-phenylenediamine (DDPBPD).

### Materials and Method

All the chemicals used were of Analar grade. DMF, ethanol and methanol were used after distillation. 4,4'-Dihydroxy-3,3'-dipropylbiphenyl (DDPB) was prepared by

Friedel-Crafts reaction. Manganese(III) acetate dehydrate was prepared<sup>3</sup> by the oxidation of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ .

#### *Preparation of ligand*

The ligand DDPBPD was prepared by refluxing a mixture of DDPB and *o*-phenylenediamine in 1:1 molar ratio in dry ethanol for 3 h. The resulting pale yellow solid was filtered and washed several times with hot water followed by ethanol and air dried. The product was insoluble in water and common organic solvents but soluble in hot DMF. The product was crystallised from hot DMF. The purity of the ligand was checked by tlc. Yield (5.0 g, 68 %), m p 322 °C.

#### *Synthesis of polychelates*

A solution of DDPBPD (0.01 mol) was prepared in DMF (25 ml), a suspension of the metal salts [ $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ , ferric chloride, vanadyl sulphate, zirconyl chloride and nitrates of Th and  $\text{UO}_2$ ] in DMF-EtOH (1 : 4 v/v) (0.01 mol, in 25 ml) were added dropwise with constant stirring. A saturated solution of ammonium acetate was also then added with rapid stirring. On refluxing the mixture on a water bath for 6-7 hours, solid were separated out, washed with hot water, DMF, EtOH and acetone and dried over fused  $\text{CaCl}_2$ .

Carbon, hydrogen and nitrogen analyses of the ligand and polychelates were carried out on a Carlo Erba 1108 at microanalytical section Central Drug Research Institute, Lucknow. The metal content of the polychelates were determined volumetrically and gravimetrically<sup>4</sup> (using a mixture of concentrated hydrochloric, nitric, per chloric and sulphuric acids) IR spectra in KBr pellets were recorded on a Perkin-Elmer 842 IR spectrophotometer. Electronic spectra were recorded on a PAS-2 spectrophotometer at BARC Mumbai. The magnetic susceptibility measurements were carried out at room temperature by the Gouy method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as a calibrant. The diamagnetic correction were taken from a standard source. Thermogravimetric analysis was performed on a Perkin-Elmer TGS-2 thermobalance with heating rate  $10^\circ \text{ min}^{-1}$  in air atmosphere at RSIC, Nagpur. For the electrical conductivity measurements a pellet of the polymer under study was prepared by pressing a finely powdered and dried sample under hydrostatic pressure at 20,000  $\text{lb in}^{-2}$  for two min. A uniform thin layer of silver paste was applied to both sides of the pellet, providing electrical contacts. The average diameter and thickness of each pellet were measured. The pellet was firmly pressed between two circular metal discs functioning as electrodes. The other ends of the electrodes were passed through the pellet holder for connections. The entire assembly was placed in furnace. It was

heated at a rate of  $1\text{ }^{\circ}\text{C min}^{-1}$ . The resistance of the pellet was measured by Zentech 702 A high resistance meter.

### Results and Discussion

All the polychelates are coloured amorphous solids, insoluble in water and common organic solvents. The analysis of the compounds agrees with expected 1:1 (metal: ligand) composition. The solids do not melt sharply but with decomposition. All the chelates are stable in air for extended periods of time.

In the IR spectra of ligand medium broad band at  $3237\text{ cm}^{-1}$  due to intramolecularly hydrogen bonded OH stretch, disappeared in the spectra of all polychelates indicating that the deprotonation of OH and its involvement in coordination<sup>5</sup>. The shift of C-O from  $1240$  to  $1280\text{ cm}^{-1}$  supports bonding of ligand through the phenolic oxygen. The ligand band at  $1638\text{ cm}^{-1}$  due to central C=N stretch, shifted to lower frequency  $1590\text{ cm}^{-1}$  on chelation confirming the coordination through azomethine nitrogen atom to the metal ions. The bands at  $970$  and  $900\text{ cm}^{-1}$  in the spectra of VO(II) and UO<sub>2</sub>(II) polychelates were attributed to V=O and O=U=O stretches respectively. New bands observed in the region  $450\text{--}650\text{ cm}^{-1}$  are assigned to M-N and M-O modes of vibration respectively<sup>6</sup>.

The Zr(IV), Th(IV) and UO<sub>2</sub>(II) polychelates are found to be diamagnetic as expected. The electronic spectra of UO<sub>2</sub>(II) polychelate exhibits charge transfer bands in the regions  $32500\text{--}33200$  and  $35300\text{--}36100\text{ cm}^{-1}$  assigned to  $n \rightarrow \pi$  and  $\pi \rightarrow \pi$  transitions respectively<sup>7,8</sup>. Low intensity band appearing around at  $20000\text{ cm}^{-1}$  shows the presence of symmetrical O=U=O stretching frequency<sup>9</sup>. The VO(II) polychelate has magnetic moment  $1.79\text{ B.M.}$  and exhibits bands at  $11764$ ,  $17182$  and  $25974\text{ cm}^{-1}$  due to  $d_{xy} \rightarrow d_{xz}$ ,  $d_{yz}$ ,  $d_{xy} \rightarrow dx^2-y^2$  and  $d_{xy} \rightarrow dz^2$  transitions, respectively, towards square pyramidal stereochemistry<sup>5</sup>. The Fe(III) polychelate shows a magnetic moment value  $5.97\text{ B.M.}$  correspondence to five unpaired electrons. The electronic spectra of this polychelate exhibits bands at  $23255$ ,  $18939$  and  $17791\text{ cm}^{-1}$ , which are assigned to the transitions  ${}^6A_{1g} \rightarrow {}^4T_{1g}$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  and  ${}^6A_{1g} \rightarrow {}^4A_{1g}$ ,  ${}^4E_{1g}$ , respectively<sup>10</sup>. From the electronic spectra and magnetic studies it is evident that Fe(III) polychelate possesses high spin octahedral configuration. The electronic spectrum of Zr (IV) polychelate exhibits single intense charge transfer band in the region  $24860\text{--}28360\text{ cm}^{-1}$  which is consistent with  $(n-1) d^{\circ} ns^0$  electronic configuration. The Mn(III) polychelate shows magnetic moment value  $4.95\text{ B.M.}$  expected for a high spin complex with four unpaired electrons. The electronic spectra of Mn(III) polychelate exhibits intense and sharp band around at  $22700\text{ cm}^{-1}$  and

another set of band in the region 12000-18520  $\text{cm}^{-1}$  are observed. The band around at 22500  $\text{cm}^{-1}$  is assigned to a charge transfer because of its high intensity. This assignment is in agreement with those of previous workers<sup>11,12</sup>. The splitting of  $d-d$  transition band in to a number of bands in the region 12000-18520  $\text{cm}^{-1}$  may be explained on the basis of a strong Jahn-Teller effect expected for a  $d^4$  ion and lowering of symmetry from octahedral.

The thermograms of these polychelates show two steps decomposition. The initial weight loss is due to the loss of two coordinated water-molecules present in the case of Fe (III), Zr (IV) and Th (IV) chelates. On further heating organic component of the chelates decompose leading to formation of metal oxide<sup>13</sup>. The activation energy was calculated from the Broido<sup>14</sup> plots of  $\ln (\ln 1/y)$  vs  $T^{-1} \times 10^3$ . Since the plots are straight lines, the rate of the reaction is believed to be one over the entire range of decomposition. The higher value of activation energy suggests the higher stability.

The d. c. electrical conductivity of ligand and its polychelates was measured in their pellet form in the temperature range 300 - 520 K. (Table 1). The electrical conductivity varies exponentially with absolute temperature according to relation  $\sigma = \sigma_0 \exp (-Ea/kT)$ , where  $\sigma_0$  is a constant,  $Ea$  is activation energy and  $k$  is the Boltzmann constant.

In all the cases electrical conductivity increases with increasing temperature indicating these chelates lie in the range of typical semiconductor<sup>15</sup>. It was observed that, there are two distinct regions. In the low temperature region the slope of plots have small values and extrinsic conduction may present in the chelates. In the high temperature region, a linear dependence of  $\log \sigma = F (1/T)$  was observed. In this temperature domain the chelates may behave as intrinsic conduction. The lower temperature range is the region of extrinsic semiconductors where the conduction of carriers from linear localized band to the conduction band. At the higher temperature range, the intrinsic region is reached where carriers are thermally activated from valence band to the conduction band. The small activation energy observed may be attributed to the interaction between the electrons on the cations and  $\pi$  orbitals of ligand. This interaction will localize the  $\pi$  electrons charge on the ligand molecules<sup>17,18</sup>.

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Table 1—Analytical, electrical and thermal data of polychelates

| Compounds   | % found (calcd)  |                |                 |                  | Decomposition Temp (°C) | Activation Energy | Electrical conductivity ( $\sigma$ ) ( $\text{ohm}^{-1} \text{cm}^{-1}$ ) | Activation energy ( $E_a$ ) (eV) |
|---|------------------|----------------|-----------------|------------------|-------------------------|-------------------|---|----------------------------------|
|   | C                | H              | N               | M                |                         |                   |   |                                  |
| $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_2$                                      | 76.41<br>(77.03) | 5.34<br>(5.94) | 07.42<br>(7.56) | ----             | 322                     | 28.20             | $9.37 \times 10^{-7}$   |                                  |
| $[\text{VO}(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)]_n$                       | 68.52<br>(69.09) | 5.05<br>(5.75) | 9.73<br>(10.07) | 11.99<br>(12.19) | 380                     | 24.14             | $7.50 \times 10^{-7}$   | 1.234                            |
| $[\text{Mn}(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)\text{OAc}]_n$             | 61.11<br>(62.48) | 4.32<br>(4.77) | 6.00<br>(6.07)  | 11.22<br>(11.91) | 374                     | 19.80             | $2.37 \times 10^{-8}$   | 0.897                            |
| $[\text{Fe}(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)(\text{H}_2\text{O})_2]$   | 61.03<br>(62.39) | 4.72<br>(4.76) | 6.01<br>(6.06)  | 11.09<br>(12.05) | 263                     | 18.17             | $7.50 \times 10^{-8}$   | 0.834                            |
| $[\text{Zr}(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)(\text{H}_2\text{O})_2]_n$ | 61.90<br>(62.44) | 4.03<br>(4.77) | 5.92<br>(6.07)  | 19.01<br>(19.07) | 352                     | 18.63             | $4.00 \times 10^{-9}$   | 0.825                            |
| $[\text{Th}(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)(\text{H}_2\text{O})_2]_n$ | 46.12<br>(47.80) | 3.07<br>(3.65) | 4.03<br>(4.65)  | 37.01<br>(38.05) | 241                     | 17.23             | $3.10 \times 10^{-10}$  | 0.469                            |
| $[\text{UO}_2(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)]_n$                     | 44.48<br>(45.07) | 3.01<br>(3.44) | 3.98<br>(4.38)  | 37.02<br>(37.08) | 247                     | 14.87             | $6.10 \times 10^{-10}$  | 0.567                            |

### References

- 1 Patel, M. M (1973) *Ind J Chem* **11** 1177
- 2 Kurimura, Y & Takato, K (1988) *J Chem Soc Faraday Trans*, **84** 841.
- 3 Christensen, O T, (1901) *Zeitschft Anorg Chem* **27** . 321
- 4 Vogel, A I (1986) *A Text Book of Quantitative Inorganic Analysis*, IV<sup>th</sup> Ed ELBS, London
- 5 Thaker, B T, Lekhadia, J., Patel, A & Thaker, P (1994) *Trans Met Chem* **19** 623
- 6 Nakamoto, K (1997) *Infrared and Raman Spectra of Inorganic and Coordination Compounds* Wiley interscience, New York
- 7 Singh, L (1997) *J Ind Council of Chemists* **12** · 690
- 8 Gouder, T R , Nadagauda, G. S & Gudassi, K B. (1993) *Ind J Chem* **32A** 1075
- 9 Maurya, R C, Mishra, D D , Pandey, M., Shukla, P. & Rathore, R. (1993) *Synth React inorg Met Org Chem* **23(1)** 161.
- 10 Patel, M. M & Patel, M R (1981) *Ind J Chem* **20A** 623
11. Thaker, B T , Patel, I A & Thaker, P B (1998) *Ind J Chem* **37 A** 429
- 12 Sharma, B C & Patel, C C (1970) *Ind J Chem* **8** . 747
- 13 Dhumwad, S D , Glllasi, K B & Gollider, I R (1994) *Ind J Chem* **33 A** 320.
- 14 Broido, A (1964) *J. Polym Sci Part A-* **217** 1761
- 15 Sutariya, D H , Patel, J R & Patel, M N (1991) *J Ind Chem Soc* **73** : 309
16. Williams, J. O. (1979) *Adv Phys Org Chem* **15** : 159.
- 17 Mmioo, L (1959) *Method of Experimental Physics*, Academic Press, New York
- 18 Patel, M M & Manavalan, R. J (1983) *J Macromol Sci. Chem* **67** · 160

## **A study on the solvation behaviour of BiBr<sub>3</sub> in MeCN, MeOH and DMF in presence of solvent ethanol**

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### **Abstract**

The nature of ion-solvent interaction involved in the system of the electrolyte BiBr<sub>3</sub> in MeCN, MeOH and DMF and the effect of addition of EtOH to it at different temperatures using electrical conductivity principle, is presented in this paper. Investigation showed the preferential solvation of the cation by the added ethanol in the case of MeCN+EtOH and DMF+EtOH mixtures. No preferential solvation by the ethanol is found in the case of MeOH+EtOH system. The limiting molar conductance of the electrolyte was determined by Kraus-Bray and Shedlovsky conductivity models. Limiting molar conductance increased in the order of EtOH<DMF<MeOH<MeCN, which is on the expected trend. Values of dissociation and association constants were also determined. The paper also reveals the energy of activation involved in the conductance process, thermodynamic parameters of association and solvation and the Walden product have been computed. From Fuoss-Accascina equation ion-pair formation constant  $K_p$  and ion triplet constant  $K_T$  were calculated and were used to support the variation in limiting conductance. Born relation was also verified. An attempt has been made to compute the solvation number using mobility method.

(**Keywords** : bismuth bromide/solvation behaviour/conductivity/Walden product)

### **Introduction**

The measurement of conductance gives important information regarding ion-solvation<sup>1,2</sup>. The study of variation of conductance with concentration, viscosity and dielectric constant provides satisfactory information not only about the behaviour of solutions but also of ion-solvation<sup>3</sup>. In recent years, there has been an increasing

interest in the behaviour of electrolytes in non-aqueous solvents with a view of investigating ion-ion and ion-solvent interactions under varied conditions<sup>4</sup>. The chemistry of bismuth is diverse<sup>5</sup>. Inorganic bismuth salts were the first compounds to be recognised for therapeutic utility<sup>5</sup>. Some compounds have been approved for human use under Federal Food, Drug and Cosmetic Act for more than 30 years<sup>5</sup>. There are no reports in literature regarding the conductivity behaviour of bismuth compounds except for some early investigations<sup>6,7</sup>. From this laboratory, we have communicated the conductance behaviour of  $\text{Bi}(\text{NO}_3)_3$  in water + DMF/DMSO<sup>8</sup>, and that of  $\text{BiBr}_3$  in MeOH/MeCN + DMF<sup>9</sup>. As an extension of it, herein, we report the solvation behaviour of  $\text{BiBr}_3$  in acetonitrile (MeCN), methanol (MeOH), dimethyl formamide (DMF), ethanol (EtOH) and their mixtures as a function of temperature.

### Materials and Methods

Dimethyl formamide (DMF), ethanol (EtOH), methanol (MeOH) and acetonitrile (MeCN) were purified as mentioned in the literature<sup>10,11</sup>. Commercially available  $\text{BiBr}_3$  (NR Chem make, Mumbai) was used as such without further purification. Solution of  $\text{BiBr}_3$  was prepared in pure solvents MeCN, MeOH, DMF and EtOH and also in the previously prepared mixtures of known composition (v/v) of MeCN/MeOH/DMF+EtOH. Since  $\text{BiBr}_3$  undergoes hydrolysis to form  $\text{BiOBr}$ <sup>12</sup>, conductivity study is impossible in water. Conductance measurements were made with a digital direct reading conductivity meter (model C M. 180, Elico make) and a dip type calibrated 8 conductivity cell with cell constant  $0.999 \text{ cm}^{-1}$ . All the measurements were made in a thermostat maintained at the desired temperature  $\pm 0.01^\circ\text{C}$ . The instrument was standardised as described<sup>8,9</sup>.

### Results and Discussion

#### *Limiting molar conductance:*

The solution of  $\text{BiBr}_3$  in various compositions of MeCN+EtOH, MeOH+EtOH and DMF+EtOH (v/v) were subjected to conductivity measurements at four different temperatures ( $288\text{--}318 \pm 0.01 \text{ K}$ ). The conductivity meter gave the specific conductance of the solution directly which was used in the determination of molar conductance ( $\Lambda_m$ ). Debye-Huckel-Onsager (DHO) equation was used to evaluate the limiting molar conductance at the initial stage. But the plot of  $\Lambda_m$  vs  $\sqrt{C}$  was non-linear and therefore did not proceed further to analyse the data by DHO equation.

Hence, Kraus - Bray equation related to 1:1 electrolyte was used since BiBr<sub>3</sub> undergoes ionisation in a solvent in the following manner<sup>13</sup>



The Kraus - Bray equation<sup>14</sup> for such systems may be represented as

$$\frac{1}{\Lambda_m} = \frac{\Lambda_m C}{K_c \Lambda_m^{02}} + \frac{1}{\Lambda_m^0} \quad (2)$$

where  $\Lambda_m^0$  is the limiting molar conductance,  $C$  is the concentration in molar and  $K_c$  is the dissociation constant. The Kraus-Bray plot was drawn for all the cases by taking  $1/\Lambda_m$  along the  $Y$ -axis and  $\Lambda_m C$  along the  $X$ -axis, and the plots were found to be linear. From the intercept and slope of the above linear plot (Fig. 1) the limiting molar conductance ( $\Lambda_m^0$ ) and dissociation constant ( $K_c$ ) were obtained and are shown in Table (1 and 2) respectively. The measurements were made at four different temperatures and at compositions of (v/v) MeCN/MeOH/DMF+EtOH (0, 20, 40, 60, 80 and 100% EtOH). The limiting molar conductance obtained are not absolute as it does not account for the effect of ionic mobility and activity coefficient on conductivity. Therefore, Shedlovsky model<sup>14</sup> was tried, which accounts for the above facts, and hence expected to give absolute limiting conductance. The Shedlovsky equation may be represented as,

$$\frac{1}{S\Lambda_m^0} = \frac{f_{\pm}^2 S K_a C \Lambda_m}{\Lambda_m^{02}} + \frac{1}{\Lambda_m^{02}} \quad (3)$$

where

$$S = \left\{ \frac{\beta \sqrt{C \lambda_m}}{2 \lambda_m^{0 \ 3/2}} + 1 + \frac{\beta^2 C \lambda_m}{4 \lambda_m^{0 \ 3}} \right\}^2$$

$$\log f_{\pm} = \frac{-1.8246 \times 10^6 (C\alpha)^{1/2} / (\epsilon T)^{3/2}}{1 + 50.24 \times 10^8 R (C\alpha)^{1/2} / (\epsilon T)^{1/2}};$$

$$\beta = \frac{8.20 \times 10^5 \lambda_m^0}{(\epsilon T)^{3/2}} + \frac{82.5}{\eta(\epsilon T)^{1/2}}$$

$$\alpha = S\lambda_m/\lambda_m^0 ;$$

$$R = q = e^2/2\epsilon kT$$

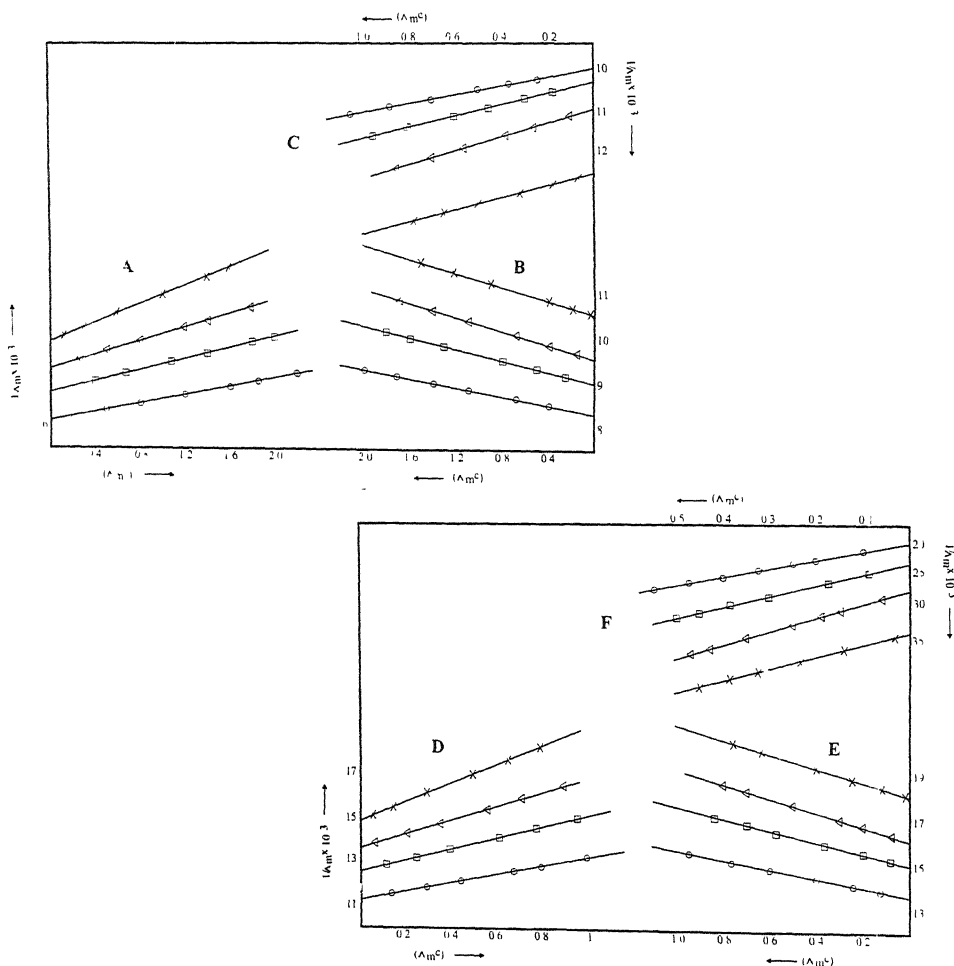


Fig 1-Plot of  $1/\Lambda_m$  (ohm .cm<sup>2</sup> mol<sup>-1</sup>)  $V_s$  ( $\Lambda_m C$ ) (mho cm<sup>-1</sup>) for BiBr<sub>3</sub> in MeCN+EtOH system.

A. 100% MeCN, B . 80% MeCN, C. 60% MeCN, D. 40% MeCN, E. 20% MeCN,  
F. 0% MeCN (100% EtOH), x 288K; Δ11298 K; □ 0308 K, O 318 K.

where  $K_a$  is the association constant and  $f_{\pm}$  is the mean ionic activity coefficient of the electrolyte. From the intercept and slope of the linear plot of  $1/S\Lambda_m$  vs  $C\Lambda_m S f_{\pm}^2$ , the limiting conductance and the association constant ( $K_a$ ) were determined. These values are shown respectively in Tables 1 and 2.  $\Lambda_m^0$  values obtained by both the models are almost the same.

Table 1– Experimental molar conductance ( $\Lambda_m^0$  mho cm<sup>2</sup> mol<sup>-1</sup>) at infinite dilution for BiBr<sub>3</sub> from different models in various solvent compositions (v/v) of MeCN/MeOH/DMF+EtOH at-

| T(K)                   | 0   |     | 20  |     | 40  |                    | 60 |    | 80 |    | 100% EtOH |    |
|------------------------|-----|-----|-----|-----|-----|--------------------|----|----|----|----|-----------|----|
|                        | 1   | 2   | 1   | 2   | 1   | 2                  | 1  | 2  | 1  | 2  | 1         | 2  |
| <div>MeCN + EtOH</div> |     |     |     |     |     |                    |    |    |    |    |           |    |
| 288                    | 126 | 126 | 96  | 96  | 79  | 79                 | 65 | 65 | 55 | 55 | 29        | 30 |
| 298                    | 138 | 138 | 106 | 106 | 89  | 89                 | 72 | 72 | 60 | 60 | 34        | 35 |
| 308                    | 147 | 147 | 111 | 111 | 96  | 96                 | 82 | 82 | 65 | 65 | 42        | 42 |
| 318                    | 163 | 163 | 122 | 122 | 100 | 100                | 89 | 89 | 74 | 74 | 49        | 49 |
| <div>MeOH+EtOH</div>   |     |     |     |     |     |                    |    |    |    |    |           |    |
| 288                    | 115 | 115 | 77  | 77  | 67  | 67                 | 54 | 55 | 49 | 49 | 29        | 30 |
| 298                    | 128 | 128 | 91  | 91  | 83  | 83                 | 67 | 69 | 56 | 57 | 34        | 35 |
| 308                    | 139 | 139 | 111 | 111 | 91  | 91                 | 74 | 76 | 61 | 61 | 42        | 42 |
| 318                    | 147 | 147 | 125 | 125 | 105 | 105                | 83 | 85 | 67 | 67 | 49        | 49 |
| <div>DMF+EtOH</div>    |     |     |     |     |     |                    |    |    |    |    |           |    |
| 288                    | 45  | 46  | 43  | 43  | 42  | 42                 | 41 | 41 | 37 | 37 | 29        | 30 |
| 298                    | 51  | 53  | 50  | 50  | 49  | 49                 | 47 | 47 | 40 | 40 | 34        | 35 |
| 308                    | 57  | 58  | 56  | 56  | 54  | 55                 | 53 | 53 | 47 | 47 | 42        | 42 |
| 318                    | 67  | 67  | 63  | 63  | 60  | 61                 | 59 | 59 | 53 | 53 | 49        | 49 |
| 1. Kraus-Bray Model    |     |     |     |     |     | 2 Shedlovsky Model |    |    |    |    |           |    |

Table 2- Experimental values of  $K_c$  and  $K_a$  for  $\text{BiBr}_3$  in various compositions of MeCN/MeOH/DMF+EtOH at-

| $T(\text{K})$ | $K_c \times 10^{-2}$ |     |     |     |     |      | $K_a$ |      |      |      |       |      |
|---------------|----------------------|-----|-----|-----|-----|------|-------|------|------|------|-------|------|
|               | 0                    | 20  | 40  | 60  | 80  | 100% | 0     | 20   | 40   | 60   | 80    | 100% |
| MeCN + EtOH   |                      |     |     |     |     |      |       |      |      |      |       |      |
| 288           | 16.4                 | 8.0 | 7.7 | 9.7 | 4.6 | 4.0  | 13.3  | 24.6 | 39.4 | 21.8 | 72.3  | 61.2 |
| 298           | 13.7                 | 8.3 | 7.1 | 9.3 | 5.4 | 5.7  | 11.6  | 20.1 | 38.9 | 22.9 | 56.1  | 36.3 |
| 308           | 13.2                 | 9.1 | 6.6 | 9.2 | 7.7 | 5.0  | 10.2  | 14.1 | 30.5 | 27.9 | 27.1  | 34.7 |
| 318           | 12.9                 | 9.2 | 9.4 | 8.9 | 7.3 | 5.0  | 9.7   | 13.7 | 25.8 | 30.2 | 22.6  | 29.7 |
| MeOH+EtOH     |                      |     |     |     |     |      |       |      |      |      |       |      |
| 288           | 2.9                  | 5.4 | 5.9 | 6.3 | 2.9 | 4.0  | 76.3  | 33.1 | 29.6 | 60.4 | 66    | 61.2 |
| 298           | 3.2                  | 4.5 | 3.9 | 4.2 | 3.2 | 5.7  | 75.1  | 43.4 | 41.3 | 65.1 | 77    | 36.3 |
| 308           | 3.5                  | 3.8 | 3.4 | 4.0 | 3.8 | 5.0  | 64.3  | 61.7 | 48.6 | 70.9 | 62    | 34.7 |
| 318           | 4.1                  | 3.4 | 3.7 | 4.1 | 4.4 | 5.0  | 43.5  | 67.6 | 61.5 | 75.6 | 48    | 29.7 |
| DMF+EtOH      |                      |     |     |     |     |      |       |      |      |      |       |      |
| 288           | 6.1                  | 7.1 | 4.6 | 2.8 | 2.0 | 4.0  | 30.1  | 21.0 | 31.5 | 66.4 | 110.3 | 61.2 |
| 298           | 5.6                  | 6.8 | 4.4 | 2.7 | 2.4 | 5.7  | 33.4  | 29.4 | 34.0 | 64.5 | 78.9  | 36.3 |
| 308           | 5.2                  | 6.2 | 4.2 | 3.1 | 2.6 | 5.0  | 34.3  | 31.8 | 41.1 | 61.5 | 78.5  | 34.7 |
| 318           | 4.9                  | 5.8 | 4.1 | 3.6 | 2.7 | 5.0  | 37.5  | 31.2 | 36.7 | 43.2 | 62.4  | 29.7 |

From Table 1, it is clear that temperature enhances the conductivity for all compositions of MeCN/MeOH/DMF+EtOH. As expected,  $\Lambda_m^0$  increased with increase in temperature in all the cases due to increase in thermal energy and mobility of ions. Inspection of Table 1 reveals that the limiting molar conductance in pure solvents varies in the order MeCN > MeOH > DMF > EtOH. According to Walden<sup>15</sup> conductivity and viscosity are inversely related, i.e. higher the conductivity lower will be the viscosity. The viscosity of these solvents varies in the reverse order as

expected. Size of the solvent molecule is another reason for such variation in conductivity. The conductivity data clearly tells that acetonitrile is a better solvent and ethanol is the least preferred solvent as far as the dissolution and dissociation of BiBr<sub>3</sub> is concerned.

Table 1 also shows that addition of EtOH either to MeCN, MeOH or DMF decreases electrical conductivity continuously till the system becomes pure ethanol medium. The decrease in conductivity is sharp in the case of MeCN+EtOH and MeOH + EtOH, whereas the variation is small in the case of DMF+EtOH. Sharp decrease in conductivity is observed from 0 to 20% EtOH in the case of MeCN/MeOH+EtOH system. This trend is similar to the one observed in the case of addition of DMF to MeOH or MeCN<sup>9</sup>. This decrease hints at the increased ion-solvent interaction and also the solvent solvent interaction in the system. The addition of EtOH leads to solvent-solvent interaction forming increased solvent mixture molecular size and which is involved in solvation of the cation. Hence here we find both the ion-solvent and solvent-solvent interactions. The magnitude of solvent-solvent interaction can be determined by its density and viscosity value. They have been measured at different temperatures and reported in Table 3. Experimental density and viscosity values of pure solvents are in agreement with the literature values<sup>16</sup> which are shown in bracket in Table 3. As is evident from Table 3 the viscosity increased with the increase in % compositions of EtOH and decreased with temperature in all the three cases of solvent mixtures. The presence of electrolyte will increase the viscosity further for any of the solvent mixtures or that of pure solvents. Therefore, conductance decreases from one composition to another at a given temperature. Sharp increase in viscosity is observed from 80% to 100% EtOH leading to sharp decrease in conductivity. From Table 1 it may also be inferred that EtOH preferentially solvates the ionic species of the electrolyte. In the case of DMF + EtOH, the viscosity decreases with increase in temperature, whereas the conductivity increases. But very marginal variation is observed from 0 to 80% EtOH indicating the least solvent-solvent interaction. But after 80% EtOH (which is ethanol rich region), the conductance decreases indicating higher ion-solvent interaction. That means, here it appears either no or negligible amount of solvent-solvent interaction. Probably, ethanol does not preferentially solvate the ionic species. The increased ion solvent interaction is found only after 60% EtOH.

*Dissociation / Association Constants :*



Table 3- Experimental values of density ( $d$  · gm/cm<sup>3</sup>) and viscosity ( $\eta$  milli poise) for MeCN/MeOH/DMF+EtOH at-

| %EtOH     | 288K   |        | 298K   |         | 308K   |        | 318K   |        |
|-----------|--------|--------|--------|---------|--------|--------|--------|--------|
|           | $d$    | $\eta$ | $d$    | $\eta$  | $d$    | $\eta$ | $d$    | $\eta$ |
| MeCN+EtOH |        |        |        |         |        |        |        |        |
| 0         | 0.7940 | 4.183  | 0.7899 | 3.652   | 0.7715 | 3.398  | 0.7607 | 3.225  |
|           |        |        |        | (3.55)  |        |        |        |        |
| 20        | 0.7880 | 4.497  | 0.7800 | 3.933   | 0.7683 | 3.707  | 0.7600 | 3.400  |
| 40        | 0.7898 | 4.767  | 0.7819 | 4.107   | 0.7705 | 3.717  | 0.7603 | 3.422  |
| 60        | 0.7961 | 6.290  | 0.7870 | 5.126   | 0.7740 | 4.627  | 0.7645 | 4.081  |
| 80        | 0.7975 | 9.102  | 0.7875 | 7.461   | 0.7771 | 6.117  | 0.7692 | 5.636  |
| 100       | 0.8005 | 14.200 | 0.7934 | 11.400  | 0.7831 | 9.446  | 0.7739 | 7.655  |
| MeOH+EtOH |        |        |        |         |        |        |        |        |
| 0         | 0.7856 | 6.244  | 0.7865 | 5.422   | 0.7772 | 4.742  | 0.7670 | 4.174  |
|           |        | (6.25) |        | (5.50)  |        | (4.8)  |        | (4.15) |
| 20        | 0.8014 | 7.652  | 0.7916 | 6.321   | 0.7821 | 5.414  | 0.7725 | 4.851  |
| 40        | 0.8039 | 9.175  | 0.7969 | 7.535   | 0.7868 | 6.437  | 0.7784 | 5.703  |
| 60        | 0.8074 | 11.600 | 0.8019 | 9.183   | 0.7919 | 7.890  | 0.7835 | 6.643  |
| 80        | 0.8153 | 14.040 | 0.8091 | 11.300  | 0.7981 | 8.873  | 0.7892 | 7.641  |
| 100       | 0.8007 | 14.200 | 0.7934 | 11.400  | 0.7831 | 9.446  | 0.7739 | 7.655  |
| DMF+EtOH  |        |        |        |         |        |        |        |        |
| 0         | 0.9559 | 9.440  | 0.9443 | 7.937   | 0.9361 | 7.167  | 0.9283 | 6.413  |
|           |        |        |        | (7.960) |        |        |        |        |
| 20        | 0.9298 | 9.490  | 0.9190 | 7.966   | 0.9084 | 7.241  | 0.8998 | 6.499  |
| 40        | 0.8975 | 9.650  | 0.8895 | 8.037   | 0.8784 | 7.278  | 0.8703 | 6.559  |
| 60        | 0.8665 | 9.985  | 0.8581 | 8.384   | 0.8460 | 7.365  | 0.8372 | 6.660  |
| 80        | 0.8310 | 11.400 | 0.8248 | 9.099   | 0.8149 | 7.949  | 0.8070 | 7.349  |
| 100       | 0.8007 | 14.200 | 0.7934 | 11.400  | 0.7831 | 9.449  | 0.7739 | 7.655  |
|           |        |        |        | (11.30) |        | (9.30) |        |        |

The electrolyte BiBr<sub>3</sub> dissociates as shown in above equation. The calculated dissociation constant ( $K_c$  from Kraus-Bray) and association constant ( $K_a$  from Shedlovsky) values are shown in Table 2.  $K_c$  value decreased with the increase in temperature from 0-40% EtOH in DMF + EtOH system and increases there onwards. At 100% EtOH, it remained almost a constant. In the case of MeCN + EtOH system, the decrease in  $K_c$  is found at all compositions except at 20% and 80% EtOH with temperature. In MeOH+EtOH system increase is found at 0 and 80% EtOH and decrease at other % compositions with increase in temperature. It may be proposed that in some cases the system behaves like endothermic and in some other cases like exothermic process.  $K_c$  decreases from 0 to 80% except at 20% and 100% EtOH in DMF+EtOH system. The  $K_a$  increases from 0 to 80% in almost all the cases at a given temperature and finally decreased at 100% EtOH. Probably, the self association<sup>2</sup> of the solvent molecule brings about caged structure in the system capturing the conducting species of the electrolyte leading to the decrease in conductance. Similar trend is observed in the case of MeCN+EtOH system. The trend in variation of  $K_a$  at a given temperature in MeOH+EtOH system is quite different. Here  $K_a$  decreases for the initial addition of EtOH to MeOH (up to 40%) with a further increase in  $K_a$  till 80%.  $K_a$  values were used to calculate change in enthalpy, free energy and entropy of the association process. The  $K_c$  increased and  $K_a$  decreased in the order of MeOH<EtOH<DMF<MeCN.

Plot of  $\log \Lambda_m$  vs  $\log C$  was drawn on the basis of Fuoss equilibrium<sup>17</sup>, to prove that the association is predominating over dissociation process, which expects a slope of the linear plot around -0.5. In the present case slope value is more than -0.5. Therefore Fuoss-Kraus equation<sup>18</sup> (eqn. 4) was used to prove further the presence of ion-pair association. where  $g(c)$  is a factor which incorporates all inter ionic interaction terms  $K_p$  and  $K_T$  are the

$$\Lambda C g(C) \sqrt{C} = \frac{\Lambda_m^0}{K_p^{1/2}} + \frac{(\Lambda_m^0)^T K_T}{K_p^{1/2}} \left( 1 - \frac{\Lambda}{\Lambda_m^0} \right) C$$

ion pair and triple ion pair formation constants and  $(\Lambda_m^0)^T$  is the limiting molar conductance of the triple ion. The values of ion pair formation constant  $K_p$  and ion triplet formation constant  $K_T$  were obtained respectively from the intercept and slope of the linear plot obtained from  $\Lambda_m \sqrt{C}$  vs  $[1 - \Lambda_m / \Lambda_m^0] C$ . The value of  $K_p$  is found higher than  $K_T$  at all compositions at 298K in all the solvent mixtures (Table 4).

Moreover, a striking feature in this case is an increase in the value of  $K_p$  and decrease in the value of  $K_T$  from 20% to 80% EtOH. So the decrease in  $\Lambda_m^0$  from 0-100% EtOH in all the cases can also be explained on the basis of  $K_p$  or  $K_T$  variation. This ideal trend is not observed in the case of pure solvents.

Table 4— Experimentally determined values of  $K_p$  and  $K_T$  for  $\text{BiBr}_3$  in MeCN/MeOH/DMF+EtOH mixture at 25°C.

| %EtOH               | $K_p$  |                     |        | $K_T$               |       |       |
|---------------------|--------|---------------------|--------|---------------------|-------|-------|
|                     | 1      | 2                   | 3      | 1                   | 2     | 3     |
| 0                   | 74.40  | 126.50              | 125.40 | 52.65               | 17.53 | 40.14 |
| 20                  | 116.16 | 111.71              | 108.50 | 80.78               | 29.04 | 41.64 |
| 40                  | 124.54 | 120.21              | 131.73 | 69.71               | 24.84 | 27.99 |
| 60                  | 128.18 | 123.71              | 138.88 | 84.36               | 21.00 | 20.82 |
| 80                  | 135.72 | 128.52              | 151.47 | 62.05               | 19.52 | 18.63 |
| 100                 | 128.51 | 128.51              | 128.51 | 32.54               | 32.54 | 32.54 |
| 1 MeCN+EtOH mixture |        | 2 MeOH+EtOH mixture |        | 3. DMF+EtOH mixture |       |       |

#### *Thermodynamic Parameters :*

The energy of activation,  $E_a$  of the conducting rate process is calculated from the Arrhenius equation<sup>17</sup>,  $\Lambda_m^0 = Ae^{-E_a/RT}$ , where  $A$  is the frequency factor,  $R$ , the gas constant and  $T$ , the temperature on absolute scale. From the slope of the plot of  $\log \Lambda_m^0$  vs  $1/T$ ,  $E_a$  is calculated and are shown in Table 5. The variation in  $E_a$  with % composition of ethanol in anyone of the systems is almost on the expected trend. In the case of pure solvents, conductivity increases in the order, EtOH < DMF < MeOH < MeCN, where as the energy of activation increases in the reverse order. That means ideality is fully followed.  $\Delta H_a$ , the enthalpy of association is calculated from the slope of the linear plot of  $\log K_a$  vs  $1/T$  in all the cases. It is found to be positive from 0 to 40% EtOH in DMF+EtOH mixture and 0 to 60% EtOH in MeOH+EtOH mixture indicating the endothermic behaviour of the system, but in other compositions including MeCN+EtOH, the  $\Delta H_a$  is found to be negative and hence the system behaves like exothermic.  $\Delta G_a$ , the free energy of association is calculated using the

Table 5- Calculated thermodynamic parameter values for BiBr<sub>3</sub> under varying compositions (v/v) of MeCN/MeOH/DMF+EtOH

| Thermodynamic parameters                   | 0      | 20     | 40    | 60    | 80     | 100%EtOH |
|--|--------|--------|-------|-------|--------|----------|
| MeCN+EtOH                                  |        |        |       |       |        |          |
| Ea(kJ mol <sup>-1</sup> )                  | 6.4    | 6.6    | 7.1   | 7.4   | 7.5    | 11.5     |
| ΔH <sub>a</sub> (kJ mol <sup>-1</sup> )    | -10.1  | -15.3  | -11.2 | 8.9   | -29.2  | -18.2    |
| ΔS(K <sup>-1</sup> kJ mol <sup>-1</sup> )* | -0.013 | -0.027 | -0.01 | 0.058 | -0.069 | -0.03    |
| -ΔG (kJ mol <sup>-1</sup> )*               | 5.9    | 6.8    | 8.7   | 8.5   | 8.4    | 9.1      |
| MeOH+EtOH                                  |        |        |       |       |        |          |
| Ea(kJ mol <sup>-1</sup> )                  | 6.7    | 9.2    | 8.9   | 9.1   | 10.8   | 11.5     |
| ΔH <sub>a</sub> (kJ mol <sup>-1</sup> )    | 6.6    | 17.8   | 17.6  | 5.6   | -19.1  | -18.2    |
| ΔS(K <sup>-1</sup> kJ mol <sup>-1</sup> )* | 0.057  | 0.092  | 0.090 | 0.053 | -0.027 | -0.029   |
| -ΔG (kJ mol <sup>-1</sup> )*               | 10.4   | 10.6   | 9.9   | 10.9  | 10.6   | 9.1      |
| DMF+EtOH                                   |        |        |       |       |        |          |
| Ea(kJ mol <sup>-1</sup> )                  | 9.1    | 9.0    | 9.1   | 8.9   | 10.8   | 11.5     |
| ΔH <sub>a</sub> (kJ mol <sup>-1</sup> )    | 6.2    | 14.5   | 10.1  | -4.8  | -14.5  | -18.2    |
| ΔS(K <sup>-1</sup> kJ mol <sup>-1</sup> )* | 0.05   | 0.075  | 0.063 | 0.019 | -0.011 | -0.029   |
| -ΔG (kJ mol <sup>-1</sup> )*               | 9.1    | 8.9    | 9.5   | 10.5  | 11.2   | 9.1      |

\* at 308K

*Walden Product :*

Walden product<sup>19</sup> relates molar conductance at infinite dilution( $\Lambda_m^0$ ) to viscosity ( $\eta_0$ ) of the solvent as

$$\Lambda_m^0 \eta_0 = \frac{Ze_0 F}{6\pi r T} \quad (5)$$

where  $r$  is the Stoke's molecular radius. The product is calculated at all temperatures and % compositions for all the three cases. Walden product remains almost a constant within the experimental error either with increase in temperature or % compositions in DMF+EtOH system indicating the constancy in the Stoke's molecular radius. But in the case of MeCN+EtOH system, variation in conductivity has not been compensated by the variation in viscosity for a given temperature. Hence, Stoke's molecular radius does not remain the same. In MeOH+EtOH mixture the variation of Walden product is still different. It decreases with the increase in temperature at all compositions except at 20% EtOH. This decrease in the product from one composition to other is observed till about 40% EtOH with a later increase at all temperatures except at 318K. From the equation 5 it is clear that the plot of Walden product vs  $1/r$ , should be linear. This is true in the case of MeCN/MeOH+EtOH mixture.

Corrected Stoke's radii was calculated<sup>8,9</sup> using equation 6 in all the solvent mixtures and the resulted values are given in Table 6.

$$r_i = \frac{ZF^2}{6\pi N \Lambda_m^0 \eta_0} + 0.0103 + r_y \quad (6)$$

where  $r_y = 0.85 \text{ \AA}$  for dipolar unassociated solvents and  $r_y = 1.13 \text{ \AA}$  applied to protic and other associated solvents,  $N$  is Avagadro number,  $Z$  is ionic charge,  $F$  is faraday constant and  $\eta_0$  is the viscosity. There is a small variation in the radius with change in temperature as well as composition especially in the case of MeCN/MeOH+EtOH system.

Table 6— Corrected Stoke's radius (Å) of the conducting molecular species of BiBr<sub>3</sub> under varying compositions of MeCN/MeOH/DMF+EtOH at-

| T/K       | 0    | 20   | 40   | 60   | 80   | 100%EtOH |
|-----------|------|------|------|------|------|----------|
| MeCN+EtOH |      |      |      |      |      |          |
| 288       | 2.79 | 3.11 | 3.36 | 3.45 | 3.04 | 3.30     |
| 298       | 2.86 | 3.16 | 3.42 | 3.64 | 3.22 | 3.40     |
| 308       | 2.86 | 3.19 | 3.47 | 3.59 | 3.48 | 3.46     |
| 318       | 2.77 | 3.16 | 3.56 | 3.67 | 3.36 | 3.56     |
| MeOH+EtOH |      |      |      |      |      |          |
| 288       | 2.63 | 2.87 | 2.80 | 2.71 | 2.61 | 3.30     |
| 298       | 2.65 | 2.88 | 2.75 | 2.72 | 2.67 | 3.40     |
| 308       | 2.69 | 2.80 | 2.82 | 2.76 | 2.92 | 3.46     |
| 318       | 2.76 | 2.77 | 2.77 | 2.81 | 2.94 | 3.56     |
| DMF+EtOH  |      |      |      |      |      |          |
| 288       | 3.24 | 3.20 | 3.13 | 3.36 | 3.35 | 3.30     |
| 298       | 3.31 | 3.25 | 3.26 | 3.43 | 3.66 | 3.40     |
| 308       | 3.31 | 3.30 | 3.23 | 3.50 | 3.61 | 3.46     |
| 318       | 3.24 | 3.24 | 3.23 | 3.49 | 3.50 | 3.56     |

*Thermodynamics of Solvation :*

Thermodynamic parameters, enthalpy ( $\Delta H_{s-s}$ ), free energy ( $\Delta G_{s-s}$ ) and entropy ( $\Delta S_{s-s}$ ) of solvation have been calculated using Born relation<sup>19</sup>

$$\Delta G_{s-s} = - \frac{N(Z_i e_0)^2}{r_i} \left( 1 - \frac{1}{\epsilon} \right) \quad (7)$$

$$\Delta S_{s-s} = \frac{N(Z_i e_0)^2}{2r_i} \frac{1}{\epsilon^2} \frac{\delta \epsilon}{\delta T} \quad (8)$$

$$\Delta H_{s,-} = \Delta G_{s,-} + T\Delta S_{s,-} \quad (9)$$

where  $N_A$  is Avagadro Number,  $Z_i$  is the charge of the ion,  $e_0$ , the electronic charge and  $r_i$  is the corrected Stoke's radius.  $\Delta H_{s,-}$ , calculated is found to be negative (Table 7) indicating the exothermic behavior of the solvation process.  $\Delta G_{s,-}$  is found to be negative indicating the feasibility of the solvation process. The decrease in the value of  $\Delta G_{s,-}$  with increase in temperature indicates that the species prefer to remain at lower temperature, where the stability of the species is higher.  $\Delta G_{s,-}$  decreases with the increase in EtOH concentration in all the three cases of solvent mixtures in the positive direction. i.e. species try to be either in pure solvents or in solvent rich region. The plot of  $-\Delta G_{s,-}$  vs  $1/r_i$  was found linear indicating the verification of Born relation.  $\Delta S_{s,-}$  is also negative but very small compared to  $\Delta H_{s,-}$  or  $\Delta G_{s,-}$ . It decreased with the increase in the amount of ethanol at a given temperature or with increase in temperature for a given composition. That means, the disorderness and electrostriction increases with the increase in the amount of EtOH either to MeCN, MeOH or DMF.

#### *Solvation Number - So :*

The solvation number  $S_n$  of  $\text{Bi}^{3+}$  ion was calculated in four pure solvents at all temperatures using the relation,

$$S_n = \frac{\frac{4}{3}\pi r_i^3 - \frac{4}{3}\pi r_{cry}^3}{\frac{4}{3}\pi r_{sol}^3} \quad (10)$$

$r_i$  is the Stoke's corrected radius,  $r_{cry}$  is the crystallographic radius and  $r_{sol}$  is the radius of the solvent molecule.  $r_{cry}$  for  $\text{Bi}^{3+}$  was obtained from the literature<sup>20</sup>. The solvation number was found to be nearly one for all the solvents except in ethanol where it is nearing two (Table 8). So, species became bulky due to which mobility decreased and hence conductivity decreased from other solvents to ethanol for  $\text{BiBr}_3$  species at a given temperature. This is what has been observed in the present case (Table 1).

Table 7- Thermodynamics of solvation for BiBr<sub>3</sub> in various compositions of MeCN/MeOH/DMF+EtOH at

| T/K  | 0  |       |     | 20  |       |     | 40  |       |     | 60  |       |     | 80  |       |     | 100%EtOH                                     |       |     |
|--|--|-------|-----|-----|-------|-----|-----|-------|-----|-----|-------|-----|-----|-------|-----|--|-------|-----|
|  | 1  | 2     | 3   | 1   | 2     | 3   | 1   | 2     | 3   | 1   | 2     | 3   | 1   | 2     | 3   | 1  | 2     | 3   |
| MeCN+EtOH                                    |  |       |     |     |       |     |     |       |     |     |       |     |     |       |     |  |       |     |
| 288  | 242  | 0 014 | 246 | 216 | 0 014 | 220 | 200 | 0 014 | 204 | 194 | 0 016 | 199 | 220 | 0 020 | 226 | 202  | 0 022 | 209 |
| 298  | 236  | 0 014 | 241 | 213 | 0 014 | 217 | 196 | 0 015 | 201 | 184 | 0 015 | 189 | 207 | 0 020 | 213 | 196  | 0 023 | 203 |
| 308  | 235  | 0 015 | 240 | 211 | 0 015 | 216 | 194 | 0 016 | 199 | 186 | 0 018 | 192 | 192 | 0 022 | 198 | 192  | 0 028 | 201 |
| 318  | 244  | 0 016 | 249 | 213 | 0 016 | 218 | 188 | 0 016 | 194 | 182 | 0 019 | 188 | 198 | 0 024 | 206 | 186  | 0 029 | 196 |
| MeOH+EtOH                                    |  |       |     |     |       |     |     |       |     |     |       |     |     |       |     |  |       |     |
| 288  | 256  | 0 045 | 269 | 235 | 0 040 | 246 | 240 | 0 040 | 264 | 247 | 0 039 | 258 | 256 | 0 036 | 266 | 202  | 0 022 | 209 |
| 298  | 254  | 0 050 | 269 | 233 | 0 044 | 246 | 244 | 0 045 | 258 | 246 | 0 042 | 259 | 250 | 0 038 | 262 | 196  | 0 023 | 203 |
| 308  | 249  | 0 052 | 265 | 239 | 0 047 | 254 | 237 | 0 045 | 251 | 242 | 0 044 | 255 | 228 | 0 038 | 240 | 192  | 0 028 | 201 |
| 318  | 242  | 0 055 | 259 | 241 | 0 053 | 258 | 241 | 0 051 | 257 | 237 | 0 047 | 252 | 226 | 0 041 | 239 | 186  | 0 029 | 196 |
| DMF+EtOH                                     |  |       |     |     |       |     |     |       |     |     |       |     |     |       |     |  |       |     |
| 288  | 208  | 0 026 | 215 | 211 | 0 027 | 219 | 214 | 0 027 | 222 | 199 | 0 025 | 206 | 199 | 0 024 | 206 | 202  | 0 022 | 209 |
| 298  | 204  | 0 028 | 212 | 207 | 0 029 | 216 | 206 | 0 028 | 214 | 195 | 0 026 | 203 | 183 | 0 023 | 190 | 196  | 0 023 | 203 |
| 308  | 204  | 0 033 | 214 | 204 | 0 033 | 214 | 207 | 0 033 | 217 | 191 | 0 030 | 201 | 185 | 0 025 | 192 | 192  | 0 028 | 201 |
| 318  | 208  | 0 038 | 220 | 207 | 0 037 | 219 | 207 | 0 037 | 219 | 191 | 0 033 | 202 | 190 | 0 028 | 199 | 186  | 0 029 | 196 |
| 1. - $\Delta G_{ss}$ (KJ mol <sup>-1</sup> ) | 2. - $\Delta S_{ss}$ (K <sup>-1</sup> kJ mol <sup>-1</sup> ) |       |     |     |       |     |     |       |     |     |       |     |     |       |     | 3. - $\Delta H_{ss}$ (kJ mol <sup>-1</sup> ) |       |     |

Table 8- Solvation number ( $S_n$ ) of the cation of the species of  $\text{BiBr}_3$  in MeCN, MeOH, DMF and EtOH at-

| Solvent | $S_n$ |      |      |      |
|---------|-------|------|------|------|
|         | 288K  | 298K | 308K | 318K |
| MeCN    | 0.95  | 1.03 | 1.03 | 0.93 |
| MeOH    | 1.01  | 1.04 | 1.09 | 1.19 |
| DMF     | 1.06  | 1.12 | 1.12 | 1.06 |
| EtOH    | 1.40  | 1.54 | 1.62 | 1.77 |

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### References

1. Conway, B E (1981) *"Ionic Hydration in Chemistry and Biophysics"*, Elsevier Scientific Publishing Company, Amsterdam.
2. Marcus Y (1985) *"Ion Solvation"*, Wiley-Interscience, New York.
3. Burgess, J. (1999) *"Ions in Solution"*, Horwood Publishing, Chichester
4. *"Non -Aqueous Electrochemistry"*, Ed Doron Aurbach , (1999) Marcel Dekkar, Inc, Israel.
5. Glen, G. Briand & Niel Buford (1999) *Chemical Rev.* **99**(9). 260
6. Viterbo, A.Q. (1913) *Chem Abs* **7** 1851
7. Smith, D.F. (1923) *J Am Chem Soc* **45** : 360.
8. Ishwara Bhat, J. & Sreelatha. T.N (2002) *Indian J Chem.* **41A** : 2462
9. Ishwara Bhat, J. & Sreelatha. T.N. (2002) *J Indian Chem. Soc* **79** . (In press).
10. Perrin, D.D., Armarego W L.F & Perrin D.R (1961) *"Purification of Laboratory Chemical"*, Pergamon Press, New York
11. *"Vogel's Text Book of Practical Organic Chemistry"*, Longman Group, U.K. (1989) 5th ed.
12. Cotton, F A & Wilkinson, G. (1966) *"Advanced Inorganic Chemistry"*, 2nd ed , Inter-science, New York.
13. Mishra, A.K. & Tandon, K N (1974) *J Electrochem Soc* , **121**(1) : 91.

- 14 Ishwara Bhat, J. & Bindu, P (1993) *J Electrochem Soc* **42** . 103
- 15 "*Techniques of Electrochemistry*", Vol 2 (1973) Ed Ernest Yeager & Alvin, J Salkind, John Wiley & Sons, Inc, New York
- 16 Conway, B E (1952) "*Electrochemical Data*", Elsevier Pub Company, New York.
- 17 Susha, C.B & Ishwara Bhat J (1996). *Proc Nat Acad Sci India* **66(A)** . 37
- 18 Fuoss, R M. & Kraus C A (1933) *J Am Chem Soc*, **55** · 476
- 19 Bockris, J O'M, Reddy, A K.N. & Maria Gomboa-Aldeco (2000) "*Modern Electrochemistry, Fundamentals of Electrodics* ", 2A, 2nd ed , Kluwer Academic/Plenum Publishers, New York
- 20 *Modern Periodic Table*, Sargent Welch Scientific Company, Illinois- USA(1968)



# Colorimetric determination of potassium using ferroin as reagent

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## Abstract

A method for the determination of potassium is reported. Ferroin is used as a reagent in 6-10 N sulphuric acid medium which gives blue colour with potassium salt solution and the blue colour obtained has got 402 nm maximum absorbance where potassium is estimated colorimetrically in the range of 3-8-13-25 mg respectively.

(**Keywords :** colorimetric determination/potassium/ferroin)

## Introduction

Several methods of determination of potassium have been reported mostly involving the instrumental methods viz., nephelometric, gasometric, flame photometric and spectrophotometric nature. The widely used flame photometric method requires special apparatus, sensitive detectors, photomultipliers and suffers the disadvantage of the interference of other elements which is sometimes contradictory in the determination of potassium.

The method for determination of potassium reported in this paper, is a simple and direct one. The potassium bromate in solution on reaction with ferroin in 6-10 N sulphuric acid medium gives blue colour and the optical density with reference to a known standard solution is measured and the amount is calculated.

## Materials and Method

### *Reagents:*

About 0.1 N solution of potassium bromate is prepared by weighing the required amount of Analar potassium bromate (supplied by B.D.H. Ltd., England) which has

been previously dried at 120°C for two hours and making up the solution to a known volume. The solution is standardised iodometrically<sup>1</sup>.

0.025 M ferroin is prepared by dissolving 1.485 g of ortho-phenanthroline monohydrate in 100 mL of 0.025 M ferrous sulphate<sup>2</sup>.

All other reagents used are of 'AnalaR' grade.

#### *Colorimetric determination*

Desired volume of 1:1 sulphuric acid is taken in each 25 mL volumetric flask to give an overall concentration of 6N. Different volumes of potassium bromate are added and mixed with 0.05 mL ferroin reagent. The blue colour developed is stable at room temperature. The maximum absorbance of the blue colour developed is at 402 nm. The Beers law curve obtained from known standard nitrate solution is given in Fig. 1. Typical results are given in Table 1.

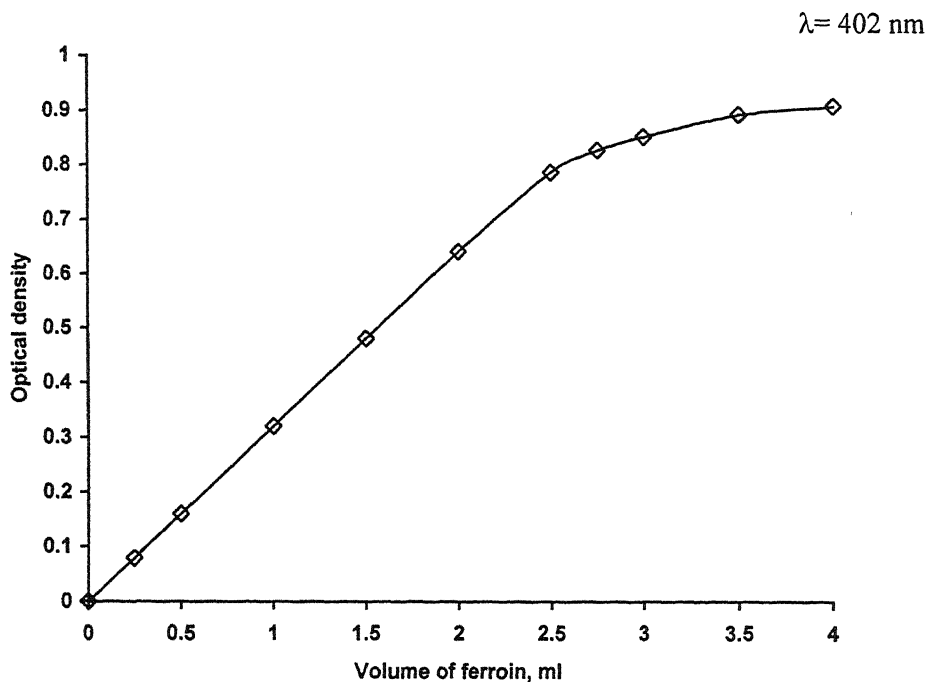


Fig. 1—Validity of Beer's law - Colorimetric determination of potassium with ferroin

Table 1—Colorimetric determination of potassium with ferroin Amount of potassium as K<sub>2</sub>O, mg

| Taken <sup>1</sup> | Found  |
|--------------------|--------|
| 3.82               | 3.804  |
| 7.361              | 7.358  |
| 10.645             | 10.648 |
| 13.250             | 13.258 |

### Results and Discussion

It is found that the acidity should be in between 6-10 N for sulphuric acid for an immediate reaction. Below 6 N the colour development is rather slow and above 10 N the colour developed gets slowly discharged. It is observed that the colour attains maximum intensity within 3 min after mixing the reagent and remains stable for 48 h, if the reagent is in excess. In the colorimetric determination, the blue colour developed is stable at room temperature. It is observed that the blue colour developed has got maximum absorbance at 402 nm. The Beer's law is obeyed upto 13.2 mg of K<sub>2</sub>O.

### References

1. Kolthoff, I M., Belcher, R., Stenger, V A & Matsuma, G (1957) *Volumetric Analysis, III*, p 506.
2. Vogel, A.I. (1969) *Quantitative Inorganic Analysis*, Longmans, London, p. 318.



## Harvesting of a prey—predator fishery with low predator density

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### Abstract

The paper deals with the combined harvesting of a prey–predator fishery with low predator density, the prey species obeying the logistic law of growth. The existence of a nontrivial steady state of the dynamical system describing the fishery is discussed. Both local and global stability of the steady state are studied. It is also examined whether the system possesses any limit cycle. Conditions for the existence of a bionomic equilibrium are established. The optimal harvest policy is discussed from the view point of control theory. The results are illustrated with the help of a numerical example. Sensitivity of the optimal solution to changes in different parameter values is then studied by using the same numerical example.

**(Keywords)** Harvesting/prey–predator fishery/bionomic equilibrium/optimal harvest policy)

### 1. Introduction

The problems related to harvesting of multispecies fisheries have drawn attention of researchers from time to time. It is always difficult, both theoretically and practically, to determine an optimal harvesting policy for the exploitation of a multispecies fishery. The difficulty actually lies in the construction of a realistic model of a multispecies system which leads to an analytically tractable optimal control problem. Carrying out dynamic optimization in problem involving more than two state variables is mathematically quite difficult. Moreover, reliable estimates of interaction coefficients are available for very few multispecies communities. In spite of these difficulties, researchers are engaged in the study of multispecies fisheries from mathematical view points. Mercer<sup>1</sup> made a survey of multispecies approaches to fishery management. Clark<sup>2</sup> devoted a separate chapter to this topic in his first book. In his second book, he discussed the prospects of bionomic modelling in the sphere of multispecies fisheries. Acknowledging the difficulties in multispecies modelling,

Clark<sup>3</sup> observed: "It should be clear that no amount of bionomic modelling is going to solve the problems of multispecies fisheries. The best that can be hoped for is that a useful classification of the issues, and perhaps some insights into appropriate management principles will emerge." Clark<sup>2</sup> discussed an optimal equilibrium policy for combined harvesting of two ecologically independent species. Mesterton-Gibbons<sup>4</sup> extended this model to discuss the optimal approach to equilibrium. Chaudhuri<sup>5,6</sup> discussed a bionomic model of nonselective harvesting of two fish species competing for an external resource supporting their growth and survival. Saha Ray and Chaudhuri<sup>7</sup> discussed a Lotka-Volterra prey-predator model with harvesting and environmental perturbations. Bionomic exploitation of a Lotka-Volterra prey-predator system was studied by Chaudhuri and Saha Ray<sup>8</sup>. The optimal policy for combined harvesting of a prey-predator community was also discussed by Mesterton-Gibbons<sup>9</sup>. In a recent paper, Mesterton-Gibbons<sup>10</sup> reconsidered the problems of Chaudhuri<sup>5,6</sup> to derive its optimal solution.

In the present paper, we have adopted a model similar to that of Smith<sup>11</sup> to describe the development of a prey-predator community in a fishery. Smeach and Rust<sup>12</sup> made a stochastic study of the model of Smith<sup>11</sup> using the mean-square theory of stochastic differential equations. However, they were not concerned with harvesting and as a consequence, they had nothing to do with bionomic analysis. We considered joint harvesting of a prey-predator community whose biological development is governed by a Smith type model<sup>11</sup>. The dynamical behaviour of the system is first studied. It is shown that a nontrivial steady state exists under certain conditions which are amenable to interpretations relevant to the model. Both local and global stability of this steady state are then discussed; existence of limit cycles is also examined. Bionomic equilibrium of the system is next discussed. We then study the optimal harvesting policy from a control-theoretical view point. A numerical example is taken up to illustrate the results. Sensitivity of the optimal solution to changes in the values of different parameters is also examined.

## 2. Statement of the Problem

Let us consider two competing fish population whose growth obey the following dynamical system :

$$\begin{aligned}\frac{dx_1}{dt} &= r_1 x_1 \left(1 - \frac{x_1}{k}\right) - \alpha x_1 x_2 = F(x_1, x_2) \\ \frac{dx_2}{dt} &= \frac{r_2 x_1 x_2}{k} - \beta x_2 = G(x_1, x_2)\end{aligned}\tag{1}$$

where  $r_1$ ,  $r_2$ ,  $\alpha$ ,  $\beta$ ,  $k$  are all positive constants.

Here  $x_1(t)$  = the size or biomass of the prey population at time  $t$ ,

$x_2(t)$  = the size or biomass of predator population at time  $t$ ,

$r_1$  = biotic potential of the prey,

$r_2$  = the maximum reproductive rate of the predator,

$\alpha$  = the rate at which the prey species is removed due to predation effects,

$\beta$  = per capita death rate of the predator,

$k$  = the carrying capacity of the prey population.

The crowding effect term (due to intra-specific competition)  $\frac{r_1 x_1^2}{k}$  is present in the first equation and it is absent in the second equation of the model. This indicates that the predator density is low; the predator species dies out exponentially in the absence of the prey.

Equations of the type (1) have been used by Smith<sup>11</sup> to model the development of a prey–predator community with low predator density.

We now assume that both the species are subjected to a combined harvesting effort governed by the differential equations:

$$\begin{aligned}\frac{dx_1}{dt} &= r_1 x_1 \left(1 - \frac{x_1}{k}\right) - \alpha x_1 x_2 - q_1 E x_1 \\ \frac{dx_2}{dt} &= \frac{r_2 x_1 x_2}{k} - \beta x_2 - q_2 E x_2\end{aligned}\tag{2}$$

where  $q_1$ ,  $q_2$  are the catchability coefficients of the two species and  $E$  denotes the effort devoted to their combined harvesting. We intend to study the characteristics of the exploited prey–predator fish species described by the dynamical system (2) and also some economic implications of the harvesting policy.

### 3. Dynamical Behaviour

(A) *Steady state :*

The steady states of the system of equations (2) are

$$P_0(0, 0), P_1(x_1^*, x_2^*), P_2(\bar{x}_1, \bar{x}_2)$$

$$\text{where } x_1^* = \frac{k}{r_1}(r_1 - q_1 E), \quad (3)$$

$$x_2^* = 0, \quad (4)$$

$$\bar{x}_1 = \frac{k(\beta + q_2 E)}{r_2}, \quad (5)$$

$$\text{and } \bar{x}_2 = \{r_1(r_2 - \beta) - E(r_1 q_2 + r_2 q_1)\} / \alpha r_2. \quad (6)$$

The nontrivial steady states of the system (2) are

$$P_1(x_1^*, x_2^*) \text{ and } P_2(\bar{x}_1, \bar{x}_2).$$

$$\text{For } x_1^* > 0, \text{ we must have from (3), that } E < \frac{r_1}{q_1}. \quad (7)$$

From (5), we have  $\bar{x}_1$  is always positive.

$$\text{It is obvious that } r_2 > \beta \quad (8)$$

$$\text{and therefore, } \bar{x}_2 > 0 \text{ iff } r_1(r_2 - \beta) > E(r_1 q_2 + r_2 q_1) \quad (9)$$

For the unexploited system ( $E = 0$ ), the nontrivial steady states  $\bar{P}_1$  and  $\bar{P}_2$  become  $\bar{P}_1(k, 0)$  and  $\bar{P}_2\left(\frac{k\beta}{r_2}, \frac{r_1(r_2 - \beta)}{\alpha r_2}\right)$ ,  $r_2 > \beta$ .

These results perfectly agree with those of Smeach and Rust<sup>12</sup> for  $\beta = 1$ . Comparing  $P_2$  with  $\bar{P}_2$ , we find that the combined harvesting effort increases the equilibrium level of the prey, but decreases that for the predator. Comparing  $\bar{P}_1$  with  $P_1$ , it is observed that, in the absence of the predator, the harvesting effort decreases the prey level.

The condition (9) may be written as :

$$0 < \frac{r_1}{q_1} + \frac{r_2}{q_2} < \frac{r_1(r_2 - \beta)}{Eq_1q_2}. \quad (10)$$

In fishery literature, the ratio of biotic potential ( $r$ ) to the catchability coefficient ( $q$ ) of a species is called its BTP (biotechnical productivity)<sup>2</sup>. Thus,  $\frac{r_1}{q_1}$  and  $\frac{r_2}{q_2}$  are the prey-BTP and the predator-BTP respectively. Condition (10) thus establishes  $\frac{r_1(r_2 - \beta)}{Eq_1q_2}$  as the maximum value of the sum of these two BTP's. When the sum of these BTP's attains the maximum value, the predator population is extinct ( $\bar{x}_2 = 0$ ). On the other hand condition (7) shows that, in the absence of predators, if the harvesting effort is equal to the prey-BTP, the prey population is extinct ( $x_1^* = 0$ ) and  $P_1$  coincides with  $P_0$ .

Condition (9) may also be rewritten as,

$$0 < E < \frac{r_1(r_2 - \beta)}{r_1q_2 + r_2q_1}. \quad (11)$$

Condition (11) defines  $E_{\max} = \frac{r_1(r_2 - \beta)}{r_1q_2 + r_2q_1}$  as the upper limit of the level of harvesting effort. We must have  $0 < E < E_{\max}$  for the existence of positive steady states of both the prey and the predator. If  $E = E_{\max} = \frac{r_1(r_2 - \beta)}{r_1q_2 + r_2q_1}$  the predator population becomes extinct ( $\bar{x}_2 = 0$ ).

## (B) Local stability

The variational matrix of the system (2) is

$$V(x_1, x_2) = \begin{bmatrix} r_1 - \frac{2r_1x_1}{k} - \alpha x_2 - q_1E & -\alpha x_1 \\ \frac{r_2x_2}{k} & \frac{r_2x_1}{k} - \beta - q_2E \end{bmatrix}.$$

$$\text{At } P_0(0, 0), V(0, 0) = \begin{bmatrix} r_1 - q_1E & 0 \\ 0 & -(\beta + q_2E) \end{bmatrix}.$$

Therefore, the eigenvalues of the variational matrix of the system (2) at  $P_0(0, 0)$  are  $r_1 - q_1E$  and  $-(\beta + q_2E)$ .

If the prey-BTP  $\frac{r_1}{q_1} > E$ , then the eigenvalue  $(r_1 - q_1E)$  is positive while the other eigenvalue is obviously negative. In this case, the equilibrium point  $P_0(0, 0)$  is a saddle point.

On the other hand, if  $\frac{r_1}{q_1} < E$ , then both the eigenvalues being real and negative,  $P_0$  is a stable node. However,  $\frac{r_1}{q_1} < E$ , makes both  $x_1^*$  and  $\bar{x}_2$  negative. In that case, no nontrivial steady state exists. We, therefore, discard the case  $\frac{r_1}{q_1} < E$  and accept (7) as the basic condition for the existence of a nontrivial steady state.

$$\begin{aligned} \text{At } P_1(x_1^*, x_2^*), V(x_1^*, x_2^*) &= \begin{bmatrix} -\frac{r_1x_1^*}{k} & -\alpha x_1^* \\ 0 & \frac{r_2x_1^*}{k} - \beta - q_2E \end{bmatrix} \\ &= \begin{bmatrix} -(r_1 - q_1E) & -\frac{\alpha k}{r_1}(r_1 - q_1E) \\ 0 & \frac{r_2}{r_1}(r_1 - q_1E) - \beta - q_2E \end{bmatrix}. \end{aligned}$$

The eigenvalues at  $P_1(x_1^*, x_2^*)$  are

$$-(r_1 - q_1 E) \text{ and } \frac{r_2}{r_1}(r_1 - q_1 E) - \beta - q_2 E.$$

Now  $-(r_1 - q_1 E) < 0$  by (7).

$$\begin{aligned} \text{If } \frac{r_2}{r_1}(r_1 - q_1 E) - \beta - q_2 E &= \frac{r_2(r_1 - q_1 E) - r_1\beta - q_2 E r_1}{r_1} \\ &= \frac{1}{r_1} \{r_1(r_2 - \beta) - E(q_2 r_1 + r_2 q_1)\} < 0, \end{aligned}$$

then  $P_1$  is a stable node. However,  $\bar{x}_2$  becoming negative in this case,  $P_2$  does not exist.

Thus,  $P_1$  is the only nontrivial steady state and it is a stable node when the reverse of the inequality (9) holds. When  $P_2$  also exists, the inequality (9) holds and the second eigen value becomes positive; as a result  $P_1$  becomes a saddle point.

The variational matrix of the system (2) at  $P_2(\bar{x}_1, \bar{x}_2)$  is

$$V(\bar{x}_1, \bar{x}_2) = \begin{bmatrix} -\frac{r_1 \bar{x}_1}{k} & -\alpha \bar{x}_1 \\ \frac{r_2 \bar{x}_2}{k} & 0 \end{bmatrix}.$$

The eigen values  $\lambda_i (i = 1, 2)$  of the system (2) at  $P_2(\bar{x}_1, \bar{x}_2)$  are the roots of the following quadratic equation in  $\lambda$  :

$$\begin{vmatrix} -\frac{r_1 \bar{x}_1}{k} - \lambda & -\alpha \bar{x}_1 \\ \frac{r_2 \bar{x}_2}{k} & -\lambda \end{vmatrix} = 0.$$

$$\text{or, } k\lambda^2 + r_1 \bar{x}_1 \lambda + \alpha r_2 \bar{x}_1 \bar{x}_2 = 0.$$

(12)

Discriminant of the equation (12) is

$$D = r_1^2 \bar{x}_1^2 - 4\alpha k r_2 \bar{x}_1 \bar{x}_2.$$

In equation (12), sum of the roots =  $-\frac{r_1 \bar{x}_1}{k} < 0$

and product of the roots =  $\frac{\alpha r_2 \bar{x}_1 \bar{x}_2}{k} > 0$ .

Therefore, the roots are either both real and negative or complex conjugates with negative real parts.

The eigen values are real or complex depending on  $D > 0$  or  $< 0$  which implies

$$E > \text{or} < \frac{4r_1 r_2 (r_2 - \beta) - r_1^2 \beta}{4r_2 (q_1 r_2 + q_2 r_1) + q_2 r_1^2} = \bar{E} \text{ (say)} \quad (13)$$

This result perfectly agrees with that of Smeach and Rust<sup>12</sup> for  $\beta = 1$  in the case of an unexploited system ( $E = 0$ ). Combining (13) with the condition on  $E_{\max}$  for the existence of the steady state ( $\bar{x}_1 \neq 0$ ,  $\bar{x}_2 \neq 0$ ), we find that

$$(a) \quad \bar{E} < E < E_{\max}$$

when the eigenvalues are real and negative and

$$(b) \quad 0 < E < \text{Min}(E_{\max}, \bar{E})$$

when the eigenvalues are complex conjugates with negative real parts.

When the eigenvalues of the system (2) are both real and negative, the non-trivial critical point  $P_2(\bar{x}_1, \bar{x}_2)$  will be an asymptotically stable node. On the other hand, the critical point  $P_2$  will be a stable focus when the eigenvalues are complex conjugates with negative real parts.

Thus, when both  $P_1$  and  $P_2$  exist, i.e. when both the inequalities (7) and (9) hold simultaneously, we find that

- (i)  $P_0$  is a saddle point;
- (ii)  $P_1$  is a saddle point;
- (iii)  $P_2$  is a stable node or a stable focus depending on the value of the effort  $E$ .

By this eigenvalue analysis, we get the behaviour of the dynamical system (2) only in the neighbourhood of the critical points.

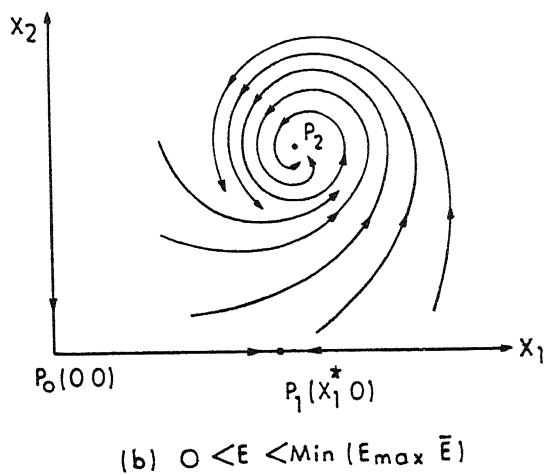
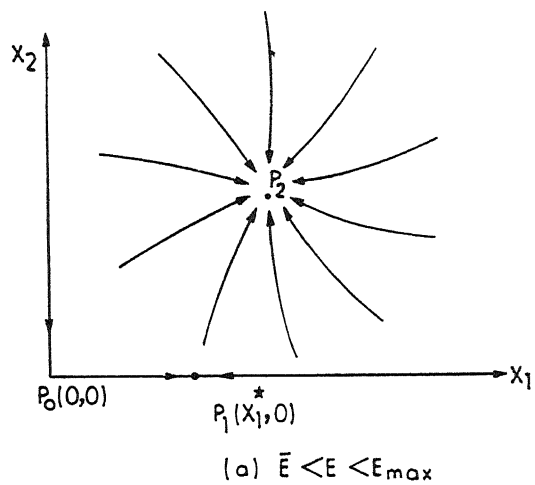


Fig 1

(C) *Limit cycle :*

The system may have a limit cycle, we now examine the possibility of existence of a limit cycle of the non-linear system (2) by using Bendixon–Dulac test in the form suggested by Clark<sup>2</sup> (p.208).

Writing the dynamical system (2) in the form

$$\begin{aligned}\frac{dx_1}{dt} &= x_1(a_1x_1 + b_1x_2 + c_1) = f(x_1, x_2) \\ \frac{dx_2}{dt} &= x_2(a_2x_1 + b_2x_2 + c_2) = g(x_1, x_2)\end{aligned}\tag{14}$$

where  $a_1 = -\frac{r_1}{k}$ ,  $b_1 = -\alpha$ ,  $c_1 = r_1 - q_1E$ ,

$$a_2 = \frac{r_2}{k}, \quad b_2 = 0, \quad c_2 = -(\beta + q_2E).$$

We find  $\Delta = a_1b_2 - a_2b_1 = \frac{\alpha r_2}{k} \neq 0$

and  $a_1c_2(b_1 - b_2) + b_2c_1(a_2 - a_1) = \frac{-\alpha r_1(\beta + q_2E)}{k} \neq 0$

$$\sigma = \frac{b_2(a_2 - a_1)}{\Delta} = 0, \quad \tau = \frac{a_1(b_1 - b_2)}{\Delta} = \frac{r_1}{r_2}.$$

Introducing the function

$$B(x_1, x_2) = x_1^{\sigma-1} x_2^{\tau-1} = x_1^{-1} x_2^{\frac{r_1}{r_2}-1},$$

we find that  $\frac{\partial}{\partial x_1}(Bf) + \frac{\partial}{\partial x_2}(Bg) = -\frac{r_1}{r_2} x_1^{-1} x_2^{\frac{r_1}{r_2}-1} (\beta + q_2E) < 0$

always in a simply connected region  $D$  in the  $x_1$ - $x_2$  plane.

Hence the expression

$$\frac{\partial}{\partial x_1}(Bf) + \frac{\partial}{\partial x_2}(Bg) \text{ does not change sign in } D.$$

Hence the system (2) does not possess limit cycles.

(D) *Global stability* :

We now examine the global stability of the dynamical system (2). We have already noted that this system has a unique positive equilibrium at  $P_2(\bar{x}_1, \bar{x}_2)$  provided the conditions (8) and (9) hold. The prey-density having a carrying capacity and the predator density being low, we may assume that the solutions of the dynamical system (2) are eventually uniformly bounded in a finite region  $B$  in the  $(x_1, x_2)$  phase plane and hence all solutions of (2) starting in  $R_2^+$  enter into the region  $B$ . We shall now prove that the interior equilibrium  $P_2(\bar{x}_1, \bar{x}_2)$  is globally asymptotically stable in the Lyapunov sense in the region  $B$ .

We define a Lyapunov function

$$V(x_1, x_2) = x_1 - \bar{x}_1 - \bar{x}_1 \ln\left(\frac{x_1}{\bar{x}_1}\right) + d\left\{x_2 - \bar{x}_2 - \bar{x}_2 \ln\left(\frac{x_2}{\bar{x}_2}\right)\right\}$$

where  $d$  is a suitable constant to be determined in the subsequent steps.

Obviously  $V$  is a positive definite function in the region  $B$  except at  $P_2(\bar{x}_1, \bar{x}_2)$  where it vanishes.

$$\text{Further } \lim_{(x_1, x_2) \rightarrow (0, 0)} V(x_1, x_2) = \lim_{(x_1, x_2) \rightarrow (\infty, \infty)} V(x_1, x_2) = \infty$$

The derivative of  $V$  along the solution of (2) is

$$\begin{aligned}
V(x_1, x_2) &= \frac{\dot{x}_1}{x_1}(x_1 - \bar{x}_1) + d \frac{\dot{x}_2}{x_2}(x_2 - \bar{x}_2) \\
&= (x_1 - \bar{x}_1) \left\{ r_1 \left( 1 - \frac{x_1}{k} \right) - \alpha x_2 - q_1 E \right\} + d(x_2 - \bar{x}_2) \left( \frac{r_2 x_1}{k} - \beta - q_2 E \right) \\
&= (x_1 - \bar{x}_1) \left[ \left\{ r_1 \left( 1 - \frac{x_1}{k} \right) - \alpha x_2 - q_1 E \right\} - \left\{ r_1 \left( 1 - \frac{\bar{x}_1}{k} \right) - \alpha \bar{x}_2 - q_1 E \right\} \right] \\
&\quad + d(x_2 - \bar{x}_2) \left[ \left( \frac{r_2 x_1}{k} - \beta - q_2 E \right) - \left( \frac{r_2 \bar{x}_1}{k} - \beta - q_2 E \right) \right] \\
&= (x_1 - \bar{x}_1) \left\{ -\frac{r_1}{k}(x_1 - \bar{x}_1) - \alpha(x_2 - \bar{x}_2) \right\} + \frac{dr_2}{k}(x_2 - \bar{x}_2)(x_1 - \bar{x}_1) \\
&= -\frac{r_1}{k}(x_1 - \bar{x}_1)^2 + \left( \frac{dr_2}{k} - \alpha \right) (x_1 - \bar{x}_1)(x_2 - \bar{x}_1) \\
&= -\frac{r_1}{k}(x_1 - \bar{x}_1)^2 < 0 \text{ provided } d = \frac{k\alpha}{r_2}.
\end{aligned}$$

Clearly  $\dot{V} = 0$  when  $x_1 = \bar{x}_1$ . On the set  $\{(x_1, x_2) : x_1 = \bar{x}_1\}$  the only invariant set is  $\{(\bar{x}_1, \bar{x}_2)\}$ . Hence by Lasalle's invariance principle<sup>13</sup>,  $P_2(\bar{x}_1, \bar{x}_2)$  is globally asymptotically stable. As a consequence of the global asymptotic stability of the equilibrium point  $P_2$  in the subspace  $B$  of  $R_2^+$ , it again follows that the system (2) has no limit cycles.

#### 4. Bionomic Equilibrium

Let,  $c$  = fishing cost per unit effort,

$p_1$  = price per unit bio-mass of the prey species

and  $p_2$  = price per unit bio-mass of the predator species.

The economic rent (net revenue) at any time is given by

$$\pi(x_1, x_2, E) = p_1 q_1 E x_1 + p_2 q_2 E x_2 - cE.$$

We find that,  $\dot{x}_1 = 0 = \dot{x}_2$  yield the results

$$\frac{r_2 x_1}{k q_2} = \frac{\beta}{q_2} + E, \quad (15)$$

$$\text{and} \quad \frac{\alpha r_2 x_2}{r_1 q_2 + r_2 q_1} = \frac{r_1(r_2 - \beta)}{r_1 q_2 + r_2 q_1} - E. \quad (16)$$

Eliminating  $E$ , we find that, the nontrivial equilibrium point of the exploited system (2) occurs at a point on the line

$$\frac{r_2 x_1}{k q_2} + \frac{\alpha r_2 x_2}{r_1 q_2 + r_2 q_1} = \frac{\beta}{q_2} + \frac{r_1(r_2 - \beta)}{r_1 q_2 + r_2 q_1}. \quad (17)$$

The biological equilibrium line (17) meets the  $x_1$  - axis and  $x_2$ -axis at  $(\tilde{x}_1, 0)$  and  $(0, \tilde{x}_2)$  respectively where

$$\tilde{x}_1 = \frac{k q_2}{r_2} \left\{ \frac{\beta}{q_2} + \frac{r_1(r_2 - \beta)}{r_1 q_2 + r_2 q_1} \right\} = \frac{k(\beta q_1 + r_1 q_2)}{r_1 q_2 + r_2 q_1} > 0$$

$$\text{and} \quad \tilde{x}_2 = \frac{(r_1 q_2 + r_2 q_1)}{\alpha r_2} \left\{ \frac{\beta}{q_2} + \frac{r_1(r_2 - \beta)}{r_1 q_2 + r_2 q_1} \right\} = \frac{\beta q_1 + r_1 q_2}{\alpha q_2} > 0.$$

The bionomic equilibrium  $(x_{1\infty}, x_{2\infty})$  of the model (2) is given by (17) together with the condition

$$\pi = (p_1 q_1 x_1 + p_2 q_2 x_2 - c)E = 0 \quad (18)$$

As long as  $(p_1 q_1 x_1 + p_2 q_2 x_2 - c) < 0$  for all points on the equilibrium line (17), the species remain unexploited because the fishery fails to produce any positive economic revenue.

The three situations that may arise with respect to the intersections of the lines (17) and (18) are given below in corresponding figures.

In Fig. 2(a), positive bionomic equilibrium exists for both the species.

In Figs. 2(b) and 2(d), the zero-profit line and the bionomic equilibrium line intersect in the second quadrant of the phase plane where  $x_{1\infty}$  is negative. Hence no bionomic equilibrium exists in these cases. Similarly, no bionomic equilibrium exists in Figs. 2(c) and 2(e) also in which the two lines intersect in the fourth quadrant where  $x_{2\infty}$  is negative.

In Figs. 2(b) and 2(c), the biological equilibrium line lies above the economic indifference line. Thus there is an economic advantage in both the cases whatever the biological equilibrium point is. It is a case of economic equilibrium only which is attained before the biological steady state is reached.

In Figs. 2(d) and 2(e), the economic indifference line lies above the biological equilibrium line. As a result, the fishermen would continue to harvest until the zero-profit lines  $\pi = 0$  is reached without caring for biological equilibrium. Thus, this is also a case of economic equilibrium only occurring beyond the biological steady state.

Solving (17) and (18), we get,

$$x_{1\infty} = \frac{k\{\alpha c - p_2(r_1 q_2 + \beta q_1)\}}{\{\alpha k p_1 q_1 - p_2(r_1 q_2 + r_2 q_1)\}} \quad (19)$$

$$x_{2\infty} = \frac{k p_1 q_1 (r_1 q_2 + q_1 \beta) - c(r_1 q_2 + r_2 q_1)}{\alpha k p_1 q_1 q_2 - p_2 q_2 (r_1 q_2 + r_2 q_1)} \quad (20)$$

Thus  $x_{1\infty}$  and  $x_{2\infty}$  are respectively given by (5) and (6) in which E is to be replaced by the bionomic effort level  $E_\infty$ . Using the open-access condition  $\pi(E_\infty) = 0$ , we get

$$E_\infty = \frac{\alpha c r_2 - \alpha \beta p_1 q_1 k - p_2 q_2 r_1 (r_2 - \beta)}{\alpha p_1 q_1 q_2 k - p_2 q_2 (r_1 q_2 + r_2 q_1)}.$$

Now  $x_{1\infty} > 0$  provided either of the following conditions holds :

$$(A) \quad p_2 > \max \left\{ \frac{\alpha c}{r_1 q_2 + \beta q_1}, \frac{\alpha k p_1 q_1}{r_1 q_2 + r_2 q_1} \right\},$$

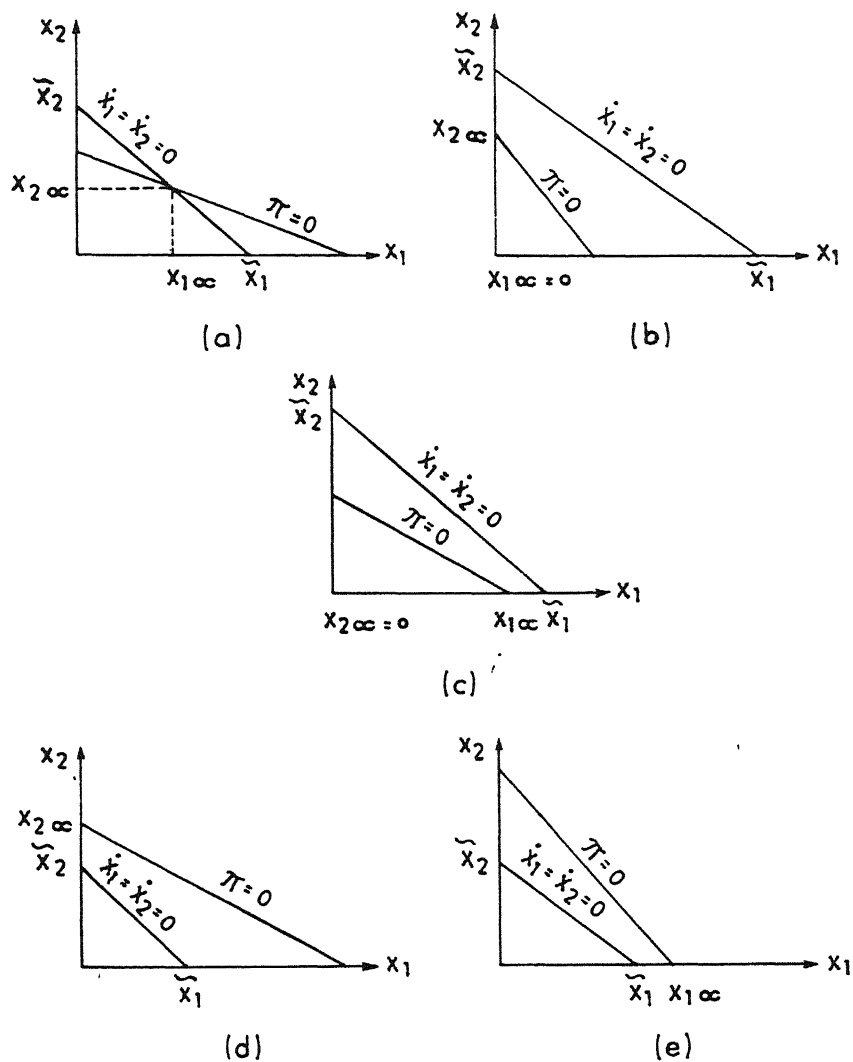


Fig. 2— Bionomic equilibrium of the prey-predator fishery

(a) Non-extinction, (b) and (d) Extinction of prey, (c) and (e) Extinction of predator

$$(B) \ p_2 < \min \left\{ \frac{\alpha c}{r_1 q_2 + \beta q_1}, \frac{\alpha k p_1 q_1}{r_1 q_2 + r_2 q_1} \right\}.$$

Similarly,  $x_{2\infty} > 0$  provided that

$$(C) \ \frac{r_1}{q_1} + \frac{r_2}{q_2} > \max \left\{ \frac{k p_1}{c} \left( r_1 + \frac{\beta q_1}{q_2} \right), \frac{\alpha k p_1}{p_2 q_2} \right\},$$

$$(D) \ \frac{r_1}{q_1} + \frac{r_2}{q_2} > \min \left\{ \frac{k p_1}{c} \left( r_1 + \frac{\beta q_1}{q_2} \right), \frac{\alpha k p_1}{p_2 q_2} \right\} \text{ holds.}$$

When either (A) or (B) and (C) or (D) hold simultaneously, both the species co-exist in bionomic equilibrium. When either (A) or (B) holds and neither (C) nor (D) holds, the predator species faces extinction in the bionomic equilibrium; the bionomic equilibrium of the fishery is supported by the prey species only. Similarly when either (C) or (D) holds and neither (A) nor (B) holds, the prey species faces extinction in the bionomic equilibrium and as a consequence, the predator population also is eventually driven to extinction.

### 5. Optimal Harvest Policy :

Our objective is to maximize the present value  $J$  of a continuous-time stream of revenues given by

$$J = \int_0^{\infty} e^{-\delta t} \{p_1 q_1 x_1 + p_2 q_2 x_2 - c\} E(t) dt \quad (21)$$

where  $\delta$  denotes the instantaneous annual rate of discount.

We intend to maximize (21) subject to the state equations (2).

The Hamiltonian for the problem is given by

$$H = e^{-\delta t} \left\{ p_1 q_1 x_1 + p_2 q_2 x_2 - c \right\} E(t) + \lambda_1 \left\{ r_1 x_1 - \frac{r_1 x_1^2}{k} - \alpha x_1 x_2 - q_1 E x_1 \right\} \\ + \lambda_2 \left\{ \frac{r_2 x_1 x_2}{k} - \beta x_2 - q_2 E x_2 \right\} \quad (22)$$

where  $\lambda_1(t)$  and  $\lambda_2(t)$  are the adjoint variables.

The adjoint equations are

$$\frac{d\lambda_1}{dt} = -\frac{\partial H}{\partial x_1} = -e^{-\delta t} p_1 q_1 E - \lambda_1 (F_{x_1} - q_1 E) - \lambda_2 G_{x_1} \quad (23)$$

$$\text{and} \quad \frac{d\lambda_2}{dt} = -\frac{\partial H}{\partial x_2} = -e^{-\delta t} p_2 q_2 E - \lambda_1 F_{x_2} - \lambda_2 (G_{x_2} - q_2 E). \quad (24)$$

We consider the optimal equilibrium solution of the given problem so that, we may write

$$E = \frac{F(x_1, x_2)}{q_1 x_1} = \frac{G(x_1, x_2)}{q_2 x_2}. \quad (25)$$

Equations (23) and (24) can be written as

$$\frac{d\lambda_1}{dt} = -e^{-\delta t} p_1 q_1 E - \lambda_1 \left( r_1 - \frac{2r_1 x_1}{k} - \alpha x_2 - q_1 E \right) - \frac{\lambda_2 r_2 x_2}{k} \quad (26)$$

$$\text{and} \quad \frac{d\lambda_2}{dt} = -e^{-\delta t} p_2 q_2 E + \lambda_1 \alpha x_1 - \lambda_2 \left( \frac{r_2 x_1}{k} - \beta - q_2 E \right). \quad (27)$$

$$\text{Equation (25) implies } r_1 - \frac{r_1 x_1}{k} - \alpha x_2 - q_1 E = 0 \quad (28)$$

$$\text{and } \frac{r_2 x_1}{k} - \beta - q_2 E = 0. \quad (29)$$

Using (28) and (29) in (26) and (27) we get

$$\frac{d\lambda_1}{dt} = -e^{-\delta t} p_1 q_1 E + \frac{\lambda_1 r_1 x_1}{k} - \frac{\lambda_2 r_2 x_2}{k} \quad (30)$$

$$\text{and } \frac{d\lambda_2}{dt} = -e^{-\delta t} p_2 q_2 E + \lambda_1 \alpha x_1. \quad (31)$$

Differentiating (30) with respect to  $t$  and using (31), we get,

$$\frac{d^2 \lambda_1}{dt^2} - \frac{r_1 x_1}{k} \frac{d\lambda_1}{dt} + \frac{r_2 \lambda_1 \alpha x_1 x_2}{k} = E e^{-\delta t} \left( \delta p_1 q_1 + \frac{r_2 x_2 p_2 q_2}{k} \right). \quad (32)$$

Auxilliary equation of (32) is

$$m^2 - \frac{r_1 x_1}{k} m + \frac{r_2 \alpha x_1 x_2}{k} = 0 \quad (33)$$

If  $m_1$  and  $m_2$  be the roots of the quadratic equation (33), then,

$$m_1 + m_2 = \frac{r_1 x_1}{k} > 0, \quad m_1 m_2 = \frac{r_2 \alpha x_1 x_2}{k} > 0.$$

Therefore, the roots of the equation (33) are both real and positive or complex conjugates with positive real parts.

*Case (i)* : When both the roots are real and unequal, the general solution of (32) is

$$\begin{aligned} \lambda_1(t) &= A_1 e^{m_1 t} + B_1 e^{m_2 t} + \frac{M_1}{N_1} e^{-\delta t} \\ \Rightarrow \lambda_1 e^{\delta t} &= A_1 e^{(m_1 + \delta)t} + B_1 e^{(m_2 + \delta)t} + \frac{M_1}{N_1} \end{aligned}$$

$$\text{where } M_1 = E \left( \delta p_1 q_1 + \frac{r_2 x_2 p_2 q_2}{k} \right),$$

$$N_1 = \delta^2 + \frac{r_1 x_1 \delta}{k} + \frac{r_2 \alpha x_1 x_2}{k}$$

and  $A_1, B_1$  are arbitrary constants.

Thus the shadow price  $e^{\delta t} \lambda_1(t)$  remains bounded as  $t \rightarrow \infty$  if  $A_1 = B_1 = 0$  and then  $e^{\delta t} \lambda_1(t) = \frac{M_1}{N_1} = \text{constant}$ .

*Case (ii) :* When the roots of the equation (33) are real but equal, each of the roots is  $\frac{r_1 x_1}{2k}$ .

The general solution of (32) is therefore,

$$\lambda_1(t)e^{\delta t} = (A_2 + B_2 t)e^{\left(\frac{r_1 x_1}{2k} + \delta\right)t} + \frac{M_1}{N_1},$$

where  $A_2$  and  $B_2$  are arbitrary constants.

In this case also, the shadow price  $\lambda_1 e^{\delta t}$  remains bounded as  $t \rightarrow \infty$  if  $A_2 = B_2 = 0$  and  $e^{\delta t} \lambda_1(t) = \frac{M_1}{N_1} = \text{constant}$ .

*Case (iii) :* When  $m_1$  and  $m_2$  are complex conjugates with positive real parts, let  $m_1 = \alpha_1 + i\beta_1$ ,  $m_2 = \alpha_1 - i\beta_1$  where  $\alpha_1 > 0$ .

The solution of (32) then becomes

$$\lambda_1(t)e^{\delta t} = A_2 e^{(\alpha_1 + \delta)t} \cos(\beta_1 t + \varepsilon) + \frac{M_1}{N_1} \text{ where } A_2 \text{ and } \varepsilon \text{ are arbitrary constants.}$$

As  $t \rightarrow \infty$  the first term becomes unbounded in an oscillatory manner. Hence the shadow price  $e^{\delta t} \lambda_1(t)$  remains bounded as  $t \rightarrow \infty$  iff  $A_2 = 0$  so that we have

$$e^{\delta t} \lambda_1(t) = \frac{M_1}{N_1} = \text{constant.}$$

In a similar manner, we can show that,  $\lambda_2(t)e^{\delta t} = \frac{M_2}{N_1} = \text{constant}$

where  $M_2 = \delta p_2 q_2 E - \alpha x_1 p_1 q_1 E + \frac{r_1 x_1 p_2 q_2 E}{k}$ .

Thus the shadow prices  $e^{\delta t} \lambda_i(t)$  ( $i = 1, 2$ ) remain constant over time in optimal equilibrium when they satisfy the transversibility condition at infinity<sup>14, 15</sup> i.e., they remain bounded as  $t \rightarrow \infty$ . Now the last condition that the Hamiltonian  $H$  must be a maximum for an admissible control  $E$  leads to the condition

$$\begin{aligned} \frac{\partial H}{\partial E} &= e^{-\delta t} (p_1 q_1 x_1 + p_2 q_2 x_2 - c) - \lambda_1 q_1 x_1 - \lambda_2 q_2 x_2 = 0 \\ \Rightarrow \lambda_1 q_1 x_1 + \lambda_2 q_2 x_2 &= e^{-\delta t} \frac{\partial \pi}{\partial E}. \end{aligned} \quad (34)$$

This shows that the total user cost of harvest per unit effort must equal the discounted value of the future price at the optimal equilibrium level.

Equation (34) can also be written as

$$\begin{aligned} q_1 x_1 \left( p_1 - \frac{M_1}{N_1} \right) + q_2 x_2 \left( p_2 - \frac{M_2}{N_1} \right) &= c \\ \text{or, } q_1 x_1 \left( p_1 - \frac{\delta p_1 q_1 + \frac{r_2 x_2 p_2 q_2}{k}}{\delta^2 + \frac{r_1 x_1 \delta}{k} + \frac{r_2 x_1 x_2 \alpha}{k}} E \right) + q_2 x_2 \left( p_2 - \frac{\delta p_2 q_2 - p_1 q_1 x_1 \alpha + \frac{r_1 x_1 p_2 q_2}{k}}{\delta^2 + \frac{r_1 x_1 \delta}{k} + \frac{r_2 x_1 x_2 \alpha}{k}} E \right) &= \end{aligned} \quad (35)$$

Eliminating  $E$  from (28) and (29), we get,

$$q_2 \left( r_1 - \frac{r_1 x_1}{k} - x_2 \alpha \right) = q_1 \left( \frac{r_2 x_1}{k} - \beta \right). \quad (36)$$

Equation (35) and (36) together determine the optimal equilibrium populations  $x_1 = x_{18}$  and  $x_2 = x_{28}$ .

## 6. Numerical Example

Let us take the parameters of the system as

$$r_1 = 0.71, r_2 = 1.8, k = 600, \alpha = 0.0009, \beta = 1, c = 100, p_1 = 250, p_2 = 500,$$

$$\delta = 0.15, q_1 = 0.0006, q_2 = 0.0007, E = 20 \text{ in appropriate units.}$$

For the given parametric values, we find that the biological equilibrium occurs at the point (338, 331) and  $\bar{E} \approx 306.26$ ,  $E_{\max} \approx 360.18$ .

Thus  $0 < E (= 20) < \min(\bar{E}, E_{\max})$ .

Therefore, criterion (b) determines that the non-trivial equilibrium point is a stable focus.

For the parametric values prescribed above, it is seen that the criteria (A) and (C) are satisfied implying that  $x_{1\infty} > 0$  and  $x_{2\infty} > 0$ . Computations using (19) and (20) actually yield  $x_{1\infty} \approx 389$  and  $x_{2\infty} \approx 119$ . It is interesting to note that the bionomic equilibrium for the prey species is established at a level higher than its biological equilibrium. On the other hand, the bionomic equilibrium for the predator occurs at a level which is much lower than its biological equilibrium. The optimal equilibrium solutions for the same numerical example obtained by solving (35) and (36) are  $x_{18} = 385$  and  $x_{28} = 134$ . Thus the optimal equilibrium solution lies between the biological equilibrium and bionomic equilibrium.

For different initial values of  $x_1(t)$ , Fig. 3 depicts the time-course display for the prey density  $x_1(t)$ . The population density  $x_1(t)$  is seen to undergo an oscillatory behaviour for smaller values to time  $t$ , whatever be the initial values  $x_1(0)$ . As  $t$  gets large, the population stabilizes at the biological equilibrium level.

Fig. 4 shows the time-course display for the predator density  $x_2(t)$  for different initial values  $x_2(0)$ . Here also  $x_2(t)$  exhibits an oscillatory behaviour for small times. Ultimately, it stabilizes to its biological equilibrium level.

The phase-plane trajectories of the dynamical system (2) are shown in Fig. 5. Clearly the biological equilibrium point  $P$  is a stable focus.

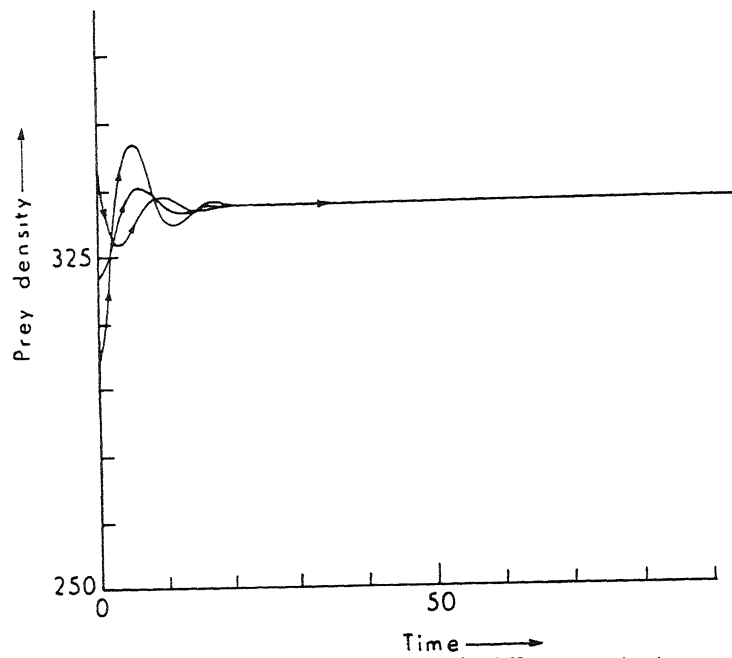


Fig 3—Time paths of the prey density for different initial values.

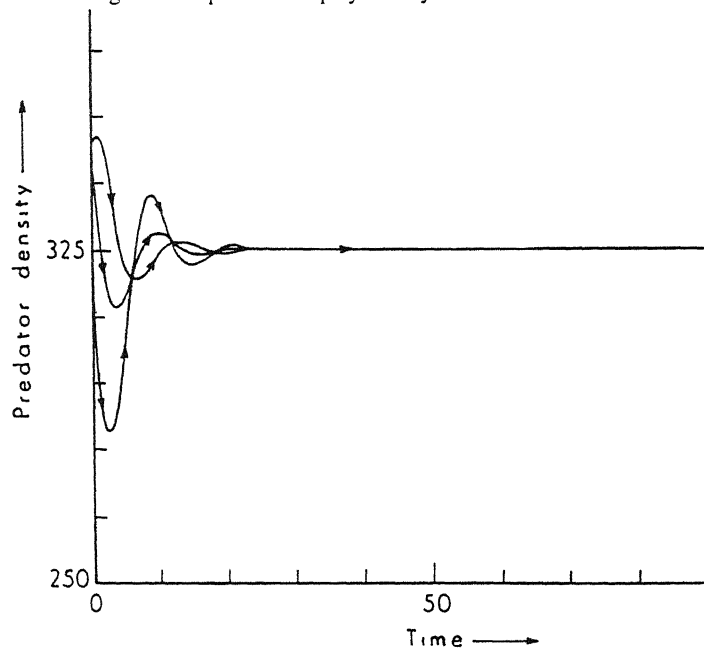


Fig 4—Time-paths of the predator density for different initial values

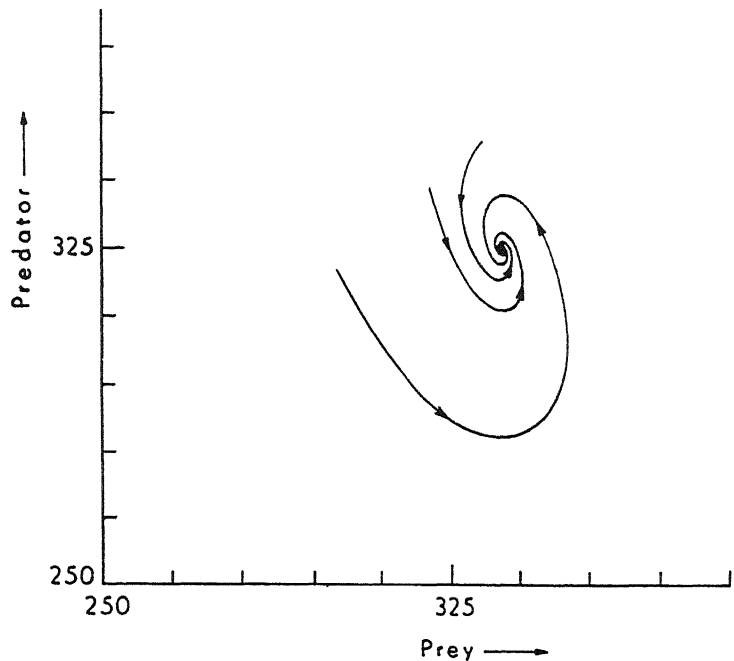


Fig 5–Phase plane trajectories of the system represented by equations (2)

7. Sensitivity Analysis

Using the above numerical example, the sensitivity analysis is performed to study the effects of changes of parameter values on the optimal solution.

Table 1– Effects of changes in the parameter values on optimal prey population and predator population

| Parameters | % change in parameters | % change in $x_{16}$ | % change in $x_{25}$ |
|------------|------------------------|----------------------|----------------------|
| $r_1$      | +30                    | 5.33                 | –6.87                |
|            | +20                    | 3.67                 | –4.72                |
|            | –20                    | –4.22                | 5.38                 |
|            | –30                    | –6.58                | 8.36                 |
| $r_2$      | +30                    | –18.67               | 23.63                |
|            | +20                    | –13.28               | 16.83                |
|            | –20                    | 18.11                | –23.25               |
|            | –30                    | 29.90                | –38.60               |

Table 2 Contd.

Table 2 Contd

|          |     |        |        |
|----------|-----|--------|--------|
| $k$      | +30 | 34.82  | -44.59 |
|          | +20 | 22.92  | -29.27 |
|          | -20 | -21.84 | 27.71  |
|          | -30 | -32.39 | 41.05  |
| $\alpha$ | +30 | -2.67  | 1.60   |
|          | +20 | -1.76  | 0.98   |
|          | -20 | 1.70   | -0.57  |
|          | -30 | 2.53   | -0.65  |
| $c$      | +30 | -6.30  | 69.49  |
|          | +20 | -4.06  | 48.88  |
|          | -20 | 4.15   | -49.95 |
|          | -30 | 6.32   | -75.98 |
| $p_1$    | +30 | 3.71   | -44.59 |
|          | +20 | 2.43   | -29.27 |
|          | -20 | -2.30  | 27.71  |
|          | -30 | -3.41  | 41.06  |
| $p_2$    | +30 | 1.96   | -23.55 |
|          | +20 | 1.42   | -17.09 |
|          | -20 | -2.21  | 26.60  |
|          | -30 | -3.86  | 46.42  |
| $\delta$ | +30 | 0.08   | -0.97  |
|          | +20 | 0.05   | -0.66  |
|          | -20 | -0.06  | 0.70   |
|          | -30 | -0.09  | 1.06   |
| $q_1$    | +30 | 0.23   | -36.70 |
|          | +20 | 0.16   | -24.36 |
|          | -20 | -0.18  | 24.09  |
|          | -30 | -0.28  | 36.05  |

Table 2 Contd

Table 2 Contd

|         |     |        |        |
|---------|-----|--------|--------|
| $q_2$   | +30 | 5.08   | -25.83 |
|         | +20 | 3.50   | -18.76 |
|         | -20 | -4.02  | 28.88  |
|         | -30 | -6.27  | 49.88  |
| $E$     | +30 | -0.28  | 3.41   |
|         | +20 | -0.19  | 2.27   |
|         | -20 | 0.19   | -2.24  |
|         | -30 | 0.28   | -3.35  |
| $\beta$ | +30 | 19.88  | -25.40 |
|         | +20 | 13.25  | -16.90 |
|         | -20 | -13.25 | 16.82  |
|         | -30 | -19.87 | 25.21  |

From the sensitivity analysis in Table – 1, the following points are observed.

- (1) both  $x_{18}$  and  $x_{28}$  are slightly sensitive to changes in the parameter  $r_1$ , the biotic-potential of the prey.  $x_{18}$  increases while  $x_{28}$  decreases with increase in  $r_1$ .
- (2) Both  $x_{18}$  and  $x_{28}$  are moderately sensitive and  $x_{28}$  is more sensitive than  $x_{18}$  to changes in  $r_2$ , the biotic-potential of the predator. Also  $x_{18}$  decreases while  $x_{28}$  increases with the increase of  $r_2$ .
- (3) Both  $x_{18}$  and  $x_{28}$  are quite sensitive and  $x_{28}$  is more sensitive than  $x_{18}$  to changes in  $k$ , carrying capacity of the prey. As  $k$  increases,  $x_{18}$  increases but  $x_{28}$  decreases.
- (4) Both  $x_{18}$  and  $x_{28}$  are insensitive to changes in  $\alpha$ , the predation coefficient.
- (5)  $x_{18}$  has very low sensitivity while  $x_{28}$  possess very high sensitivity to changes in  $c$ , the cost per unit effort. As  $c$  increases,  $x_{18}$  decreases slowly, but  $x_{28}$  increases rapidly.

- (6)  $x_{18}$  is slightly sensitive while  $x_{28}$  is highly sensitive to changes in  $p_1$ , the price per unit biomass of the prey. As  $p_1$  increases,  $x_{18}$  increases slowly, but  $x_{28}$  decreases rapidly.
- (7)  $x_{18}$  is almost insensitive while  $x_{28}$  is quite sensitive to changes in  $p_2$ , the price per unit biomass of the predator.  $x_{18}$  increases slightly but  $x_{28}$  decreases considerably as  $p_2$  increases.
- (8)  $x_{18}$  and  $x_{28}$  are almost insensitive to changes in  $\delta$ , the discount rate.
- (9)  $x_{18}$  is almost insensitive while  $x_{28}$  is considerably sensitive to changes in  $q_1$ , the catchability coefficient of the prey. As  $q_1$  increases  $x_{28}$  decreases and vice-versa.
- (10)  $x_{18}$  has low sensitivity and  $x_{28}$  has high sensitivity to changes in  $q_2$ , the catchability coefficient of the predator.  $x_{18}$  undergoes slow increase and  $x_{28}$  undergoes rapid decrease as  $q_2$  increases.
- (11)  $x_{18}$  is almost insensitive and  $x_{28}$  is slightly sensitive to changes in  $E$ , the level of harvesting effort. It should, however, be remembered that, this result holds for admissible values of  $E$  as per conditions (a) and (b).
- (12) Both  $x_{18}$  and  $x_{28}$  are quite sensitive to changes in  $\beta$ , the percapita death rate of the predator.  $x_{18}$  increases and  $x_{28}$  decreases with the increase of  $\beta$ .

## 8. Discussion

The present model is suitable for a fishery having a prey-predator community in which the prey density is high and that of the predators is low. An appropriate example might be a krill-whale fishery. For the numerical example taken here, we have determined three equilibria; biological equilibrium  $P_1(338,331)$ , bionomic equilibrium  $P_2(389,119)$  and optimal equilibrium  $P_3(385,134)$ .  $P_1$  is the most conservative of these three solutions. However, the economists may dislike it because it takes no economic factors into consideration. Although  $P_2$  is based on economic considerations, its acceptability also is questionable because the fishery is, in this case, run on the no-profit-no-loss basis.  $P_3$  seems to be the best choice for the fishery manager.

As far as the dynamical behaviour of the system is concerned, the existence of positive steady states for both the species depends primarily on their BTP's. These BTP's, on the other hand, depends on what types of fishing gear are being used, technical efficiency of the fishing gear is reflected in the catchability coefficients  $q_1$  and  $q_2$ . Thus the choice of the fishing gear is crucial for the survival of the species. The BTP's in turn, define upper and lower limits of the level of fishing effort  $E$ . These limits of  $E$  determine the behaviour of the steady state. Non-existence of any limit cycle of the system implies that the system does not undergo periodic oscillations. As we have seen in the case of local stability of the system, there are strict eigen-value inequalities: either (i)  $\lambda_1 < 0$ ,  $\lambda_2 < 0$  or (ii)  $\lambda_1, \lambda_2$  are complex and  $\text{Re } \lambda_i < 0$  ( $i = 1, 2$ ). These strict eigenvalue inequalities are preserved by small changes in the elements of the eigen matrix. Thus the stable node in case (i) and the stable focus in case (ii) are stable relative to small perturbations of the parameters  $r_1, r_2, \alpha, \beta$  and  $k$ . Hence the dynamical system (2) represents a reasonable model of a biological system. The global asymptotic stability of the steady state implies that the behaviour of the solution trajectories does not change drastically if the model is subject to small perturbations.

As we have already seen in Figs. 2(b) and 2(d), practically no bionomic equilibrium exists because (17) and (18) intersect at a point with  $x_{1\infty} < 0$ . In such a case, as Clark<sup>2</sup> (p. 305) says, the two lines do not intersect, and bionomic equilibrium occurs at the point  $(0, x_{2\infty})$ . This view is untenable because the bionomic equilibrium state is defined as the point of the state plane in which both the conditions (17) and (18) are satisfied. It is also seen from (19) that  $x_{1\infty} \rightarrow 0$  and  $x_{2\infty} \rightarrow \frac{q_1\beta + q_2r_1}{q_2\alpha}$  (a finite quantity) only when  $p_2$  is finite and  $p_1 \rightarrow \infty$ . This cannot be a practical situation. The same observation holds for the situations depicted in Figs. 2(c) and 2(e) also. Thus there cannot be any bionomic equilibrium with one species extinct as concluded by Clark<sup>2</sup>. Positive bionomic equilibria of both the species exist when  $p_1$  and  $p_2$  are both finite and other conditions, as discussed in section 4, are satisfied.

## References

- 1 Mercer, M. C. (1982) *Canad Publ Spec Fish Aquat Sci.* 59.
- 2 Clark C. W. (1976) *Mathematical Bioeconomics - The optimal management of renewable resources*, John Wiley & Sons, New York.
- 3 Clark C. W. (1985) *Bioeconomic Modelling and Fisheries Management*, John Wiley & Sons, New York.

4. Mesterton-Gibbons M (1987) *Nat Resour Model* **2** 109
5. Chaudhuri K (1986) *Ecological Modelling* **32** · 267
6. Chaudhuri K (1988) *Ecological Modelling* **41** 17
7. Saha Ray S & Chaudhuri K S (1989) *Ecological Modelling* **47** 283
8. Chaudhuri K S & Saha Ray S (1991) *Bull Cal Math Soc* **83** · 175
9. Mesterton-Gibbons M (1988) *Nat Resour Model* **3** · 63
10. Mesterton-Gibbons M (1996) *Ecological Modelling* **92** 235.
11. Smith J M (1968) *Mathematical Idea in Biology*, Cambridge University Press, London
12. Smeach S C & Rust A (1978) *Bull Math Biol* **40** · 483.
13. Hale J K (1969) *Ordinary Differential Equations*, Wiley Interscience, New York
14. Arrow K J & Kurz M (1970) *Public Investment, the Rate of Return and Optimal Fiscal Policy*, Johns Hopkins Press, Baltimore.
15. Halkin H (1974) *Econometrica* **42** 267

## Creep transition in torsion of a non-homogeneous cylinder

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### Abstract

Creep transition in a circular non-homogeneous cylinder, subjected to torsion has been studied by transition approach. Non-homogeneity in the material is considered due to radial variation of modulus of rigidity. Stresses for steady state creep have been derived and discussed numerically. Effects of the non-homogeneity appear to be prominent and the same shear stress distribution has been found for different combinations of the non-homogeneity parameter  $k$  and the measure  $n$ . Moreover, non-homogeneity of a certain type having more value at the outer radius than at the centre of the cylinder may be beneficial from a design point of view.

(**Keywords** : creep/torsion/generalised measure)

### Introduction

The 327 page paper presented to the French Academy by St. Venant<sup>1</sup>, about one and half century ago remains the most outstanding work on the torsion of cylinders of arbitrary cross-section, that, is circular, elliptical, rectangular, equilateral, triangular etc., and the topic entered many texts<sup>2-5</sup>. Lee<sup>6</sup> considered the torsion of an elastic perfectly plastic cylindrical bar and showed that the curvature of the shearing stress lines in the plastic zone has an upper bound proportional to the twisting angle, while Cho and Findley<sup>7</sup> studied creep and plastic strains under side steps to tension and torsion for 304 stainless steel at 593°C. An analysis for the creep deformation of a thin-walled cylinder subjected to axial force, bending and twisting moment, was carried out by Lau *et. al.*<sup>8</sup> under the assumptions of Prandtl-Nadai creep law and incompressibility of the material.

The problem of torsion of a semi-infinite isotropic, homogeneous, elastic solid when a circular cylinder welded to its plane boundary and is forced to rotate about its axis was first discussed by Reissner and Sagoci<sup>9</sup>. Erguven<sup>10</sup> worked on the Reissner-Sagoci problem for a transversely isotropic, non-homogeneous elastic solid by varying the modulus of rigidity as a power of the radial co-ordinate and a note on the twisting of a non-homogeneous sphere has been furnished by Chaudhuri and Datta<sup>11</sup> on the

basis of classical theory of elasticity. In an investigation Cowin<sup>12</sup> observed that for a certain class of elastic cylinders with shape intrinsic orthotropy, the solution to the torsion problem is the same as the solution to the torsion problem for the isotropic cylinder of the same shape if the isotropic shear modulus were replaced by the orthotropic cylinders by considering the finite strains incompressibility of the material and Norton's law of creep.

In this paper an attempt has been made to study creep transition in torsion of a non homogeneous cylinder with the help of transition approach. Transition theory developed by Seth<sup>14,15</sup> does not require any adhoc assumptions like incompressibility of the material or creep strain law, and solves a more general problem from which cases pertaining to such assumptions can be worked out<sup>16-23</sup>. It utilises the concept of generalised strain measure and asymptotic transition through the critical points of the differential system defining the deformed field. For uni-axial case, Seth<sup>14</sup> has defined the generalised strain measure as

$$e = (1/n \{1 - \{l_0/l\}^n\})^m \quad (1)$$

where  $n$  is the measure,  $m$  the irreversibility index,  $l_0$  and  $l$  are the initial and strained length of the rod respectively.

Here, a secondary stage of creep, i.e.,  $m=1$  has been considered and non-homogeneity in the material is taken due to radial variation of modulus of rigidity

$$\mu = \mu_0 r^{-k} \quad (2)$$

where  $\mu_0$  and  $k$  are real constants.

### Governing Equations

Considering a long circular cylinder of radius  $a$  subjected to finite twist. Let  $r, \theta, z$  refer to the radial, tangential and axial directions of the cylinder and  $z$ -axis is coincident with its long axis. The components of displacement are given by<sup>15,19</sup>

$$u = r(1-\beta), v = \alpha r z, w = d_1 z, \quad (3)$$

where  $d_1$  is a constant,  $\alpha$  is the angle of twist per unit length and  $\beta$  is a function of

$$r = (x^2 + y^2)^{1/2} \text{ only.}$$

The generalised components of strain from eqn. (1) are <sup>19,20</sup>

$$\left. \begin{aligned} e_{rr} &= 1/n [1 - (r\beta' + \beta)^n], \quad e_{\theta\theta} = 1/n [1 - \beta^n], \\ e_{zz} &= 1/n [d_2 - (\alpha r\beta)^n], \quad e_{\theta z} = 1/n (\alpha r)^{n/2} \beta^n, \\ e_{r\theta} &= e_{zr} = 0, \end{aligned} \right\} \quad (4)$$

where

$$d_2 = 1 - (1 - d_1)^n \text{ and } \beta' = d\beta/dr$$

Stress-strain relations are

$$\tau_{ij} = \lambda \delta_{ij} e_{ii} + 2\mu e_{ij}, \quad (i, j = 1, 2, 3) \quad (5)$$

where  $\tau_{ij}$  and  $e_{ij}$  are the stress and strain tensors respectively,  $\lambda$  and  $\mu$  are Lamé's constants and  $\delta_{ij}$  is Kronecker's delta.

Substituting eqn. (4) into eq. (5), one gets

$$\left. \begin{aligned} \tau_{rr} &= \lambda S_1 + 2\mu [1 - (r\beta' + \beta)^n] / n, \quad \tau_{\theta\theta} = \lambda S_1 + 2\mu [1 - \beta^n] / n, \\ \tau_{zz} &= \lambda S_1 + 2\mu [d_2 - (\alpha r\beta)^n] / n, \quad \tau_{\theta z} = 2\mu \beta^n (\alpha r)^{n/2} / n, \\ \tau_{r\theta} &= \tau_{\theta z} = 0, \end{aligned} \right\} \quad (6)$$

where  $S_1 = [2 + d_2 - \beta^n - (r\beta' + \beta)^n - (\alpha r\beta)^n] / n$ .

Equation of equilibrium to be satisfied is <sup>20</sup>

$$\partial \tau_{rr} / \partial r + (\tau_{rr} - \tau_{\theta\theta}) / r = 0 \quad (7)$$

Substituting from eqn. (6) into eqn. (7), one gets a non-linear differential eqn. in  $\beta$  as

$$\begin{aligned}
 (\lambda+2\mu)\beta P(P+1)^{n-1}dP/d\beta &= 2\mu[1-(P+1)^n]/n + 2\mu'r[\beta^n-(P+1)^n]/n \\
 &- \lambda(\alpha r)^n - P[\lambda(1+\alpha^n r^n) + (\lambda+2\mu)(P+1)^n],
 \end{aligned} \quad (8)$$

where  $r\beta' = \beta P$  and  $\mu' = d\mu/dr$

Transition points of  $\beta$  in eq. (8) are

$$P \rightarrow 0, -1, \pm \infty.$$

Torque applied is

$$M = 2\pi \int_0^a r^2 \tau_{\theta z} dr \quad (9)$$

### Statement and Mathematical Model of the Problem

Following the transition approach, we analyse the problem of creep transition in torsion of a cylinder made of the material having variable modulus of rigidity along the radius, and governed by eqn. (2), (6) to (9). It is of interest to investigate the actual variation of the creep stresses on the assumption that the radial stress vanishes on the free surface and no longitudinal force acts on transverse sections of the cylinders i.e.

$$\tau_{rr} = 0, \text{ at } r = a \quad (10)$$

$$\text{and} \quad \int_0^a 2\pi r \tau_{zz} dr = 0 \quad (11)$$

### Solution of the Problem

It has been shown by several workers<sup>19-23</sup> that the asymptotic transition through the principal stress difference gives creep stresses at the transition point  $P \rightarrow -1$ . Therefore, we take the transition function  $R_1$  as<sup>19, 21</sup>.

$$R_1 = \tau_{rr} - \tau_{\theta\theta} = 2\mu\beta^n[1-(P+1)^n]/n \quad (12)$$

Taking logarithmic differentiation of eqn. (12), with respect of  $r$ , we get

$$d/dr(\ln R_1) = \mu'/\mu + nP \{ 1 - [\beta(P+1)^{n-1}/1 - (P+1)^n] dP/d\beta \} / r \quad (13)$$

Substituting the value of  $dP/d\beta$  from eq. (8) in eq. (13) and taking the asymptotic value as

$P \rightarrow -1$ , after integration one obtains

$$R_1 = \tau_{rr} - \tau_{\theta\theta} = A_1 \mu r^{-2n} \exp f(r), \quad (14)$$

where  $A_1$  is a constant of integration and

$$f(r) = \int [(n-1)c/r - (c'/1-c)\beta^{-n}] dr, c' = dc/dr, c = 2\mu/\lambda + 2\mu$$

Substituting eqn. (14) into eqn. (7) and integrating

$$\tau_{rr} = A_2 - A_1 I_1(r), \quad (15)$$

$$\text{and } \tau_{\theta\theta} = \tau_{rr} - A_1 \mu r^{-2n} \exp f(r), \quad (16)$$

where  $A_2$  is a constant of integration and

$$I_1(r) = \int \mu r^{-2n-1} \exp f(r) dr.$$

The asymptotic value of  $\beta$ , obtained from solving eqn. (12) and (14) as

$$\beta^n = (A_1/2) n r^{-2n} \exp f(r) \quad (17)$$

In view of eqs. (6) and (17), other stresses in the cylinder are

$$\tau_{zz} = \{ (1-c)/2-c \} [ \tau_{rr} + \tau_{\theta\theta} ] + \{ 2d_2/n - A_1 S_3 \} S_2/r, \quad (18)$$

$$\text{and } \tau_{\theta z} = A_1 S_4, \quad (19)$$

where  $S_2 = \{ (3-2c)/2-c \} \mu r$ ,  $S_3 = \alpha^n r^{-n} \exp f(r)$ ,

$$S_4 = \mu \alpha^{n/2} r^{-3n/2} \exp f(r)$$

Applying bounding conditions (10) and (11) to eqn. (15) and (18), we obtain

$$A_2 = A_1 I_1(a), A_1 = -2d_2 I_2 / n I_3, \quad (20)$$

where

$$I_2 = \int_0^a S_2 dr, I_3 = \int_0^a \{ [I_1(a) - I_1(r)] r^2 c' / (2-c)^2 - S_2 S_3 \} dr$$

The twisting couple in the cylinder is given by

$$M = 2\pi A_1 \int_0^a r^2 S_4 dr \quad (21)$$

Eqn. (15), (16), (18) to (21) provide transitional stresses for stationary state of creep for a cylinder made of the material having variable modulus of rigidity, subjected to torsion.

For a cylinder having non-homogeneity in accordance with eqn. (2), the transitional creep stresses obtained by substituting eqn. (2) into eqn. (15), (16), (18) to (21) as

$$\left. \begin{aligned} \tau_{rr} &= A_3 [I_4(a) - I_4(r)], \\ \tau_{\theta\theta} &= A_3 [I_4(a) - I_4(r) - S_5], \\ \tau_{zz} &= A_3 S_6 [2I_4(a) - 2I_4(r) - S_5] + S_7 (2\mu_0 d_2 / n - A_3 \alpha^n S_8), \\ \tau_{\theta z} &= A_3 \alpha^{n/2} S_9, \quad M = 2\pi A_3 \alpha^{n/2} I_7, \end{aligned} \right\} \quad (22)$$

where

$$\begin{aligned} A_3 &= 2\mu_0 d_2 [a^{2-k}/2 - k + I_6] / n I_5, I_4(r) = \int_0^a S_5 / r dr, I_7 = \int_0^a r^2 S_9 dr, \\ I_6 &= \int_0^a [r / (2r^k + t)] dr, I_5 = \int_0^a \{ kt S_{10} [I_4(a) - I_4(r)] + \alpha^n S_{11} \} dr, \end{aligned}$$

$$\begin{aligned}
 S_5 &= r^{t_1} \exp f_1, S_6 = r^k / 2r^k + t, S_7 = (3 + tr^{-k}) / 2r^k + t, S_8 = r^{-n} \exp f_1, \\
 S_9 &= r^{t_2} \exp f_1, S_{10} = r^{k+1} / (2r^k + t)^2, S_{11} = S_7 r^{1-n} \exp f_1, t = 2\mu_0 / \lambda \\
 t_1 &= -k - 2n, t_2 = -k - 3n/2, f_1 = (n-1)t [dr/r(r^k + t) + kt/d_0^n] [r^{n-1}/r^k + t] dr, \\
 \beta &\rightarrow d_0/r, d_0 \text{ being a constant.}
 \end{aligned}$$

For an incompressible material, that is,  $\lambda \rightarrow \infty^{23, 24}$ , eqn. (22) gives

$$\left. \begin{aligned}
 \tau_{rr} &= A_4 (a^{t_1} - r^{t_1}) / t_1, \tau_{\theta\theta} = A_4 [a^{t_1} - (1 + t_1)r^{t_1}] / t_1, \\
 \tau_{zz} &= A_4 [a^{t_1} - (1 + t_1/2)r^{t_1}] / t_1 + (E_0 d_2 / n - 3A_4 \alpha^n r^{-n} / 2) r^{-k}, \\
 \tau_{\theta z} &= A_4 \alpha^{n/2} r^{t_2}, M = 2\pi A_4 \alpha^{n/2} a^{t_3} / t_3,
 \end{aligned} \right\} (23)$$

where  $\mu_0 \rightarrow E_0/3$ ,  $E_0$  is the constant value of Young's modulus,

$$t_3 = 3 + t_2, A_4 = 2(2 - k - n)E_0 d_2 a^n / 3(2 - k)n \alpha^n.$$

For homogeneous case, that is,  $k = 0$ ,  $c_0$  is a constant and eqn. (14) reduces to

$$\tau_{rr} - \tau_{\theta\theta} = A_1 r^{t_4}, \quad (24)$$

where  $t_4 = (n-1)c_0 - 2n$ .

Consequently, the transitional stresses for steady state creep become

$$\left. \begin{aligned}
 \tau_{rr} &= A_1 (a^{t_4} - r^{t_4}) / t_4, \tau_{\theta\theta} = A_1 [a^{t_4} - (1 + t_4)r^{t_4}] / t_4, \\
 \tau_{zz} &= A_1 (1 - c_0) [2a^{t_4} - (2 + t_4)r^{t_4}] / t_4 (2 - c_0) + \{3 - 2c_0\} [2\mu_0 d_2 / n - A_1 \alpha^n r^{t_5}] / 2 - c_0, \\
 \tau_{\theta z} &= A_1 \alpha^{n/2} r^{t_6}, M = 2\pi A_1 \alpha^{n/2} a^{t_7} / t_7,
 \end{aligned} \right\} (25)$$

where  $t_5 = (n-1)c_0 - n, t_6 = (n-1)c_0 - 3n/2, t_7 = 3 + t_6$ ,

$$A_1 = (2 + t_5)\mu_0 d_2 / n \alpha^n a^{t_5}.$$

### Numerical Discussion

In the specific case, calculations have been made for the shear stress ratio  $\tau = \tau_{\theta z} / M_1$ , where  $M_1 = M/2 \pi a^3$ , for different combinations of  $k$  and  $n$ , using eqn. (23). Fig. 1 shows variation of the creep shear stress ratio,  $\tau$  with radii ratio,  $R = r/a$  of the non-homogeneous incompressible cylinder under torsion. It can be observed that the shear stress is maximum at the outer radius of the cylinder for the non-homogeneity  $k < 0$  with smaller values of the measure  $n$ ,  $0 < n \leq 2/3$ . For  $k \geq 0$ , the shear stress is found to be maximum at the centre of the cylinder and its value increases abruptly at the centre with increasing  $k$  and  $n$ . However, the same shear stress distribution can be obtained for various values of  $k$  and  $n$ , and the stress remains constant through the

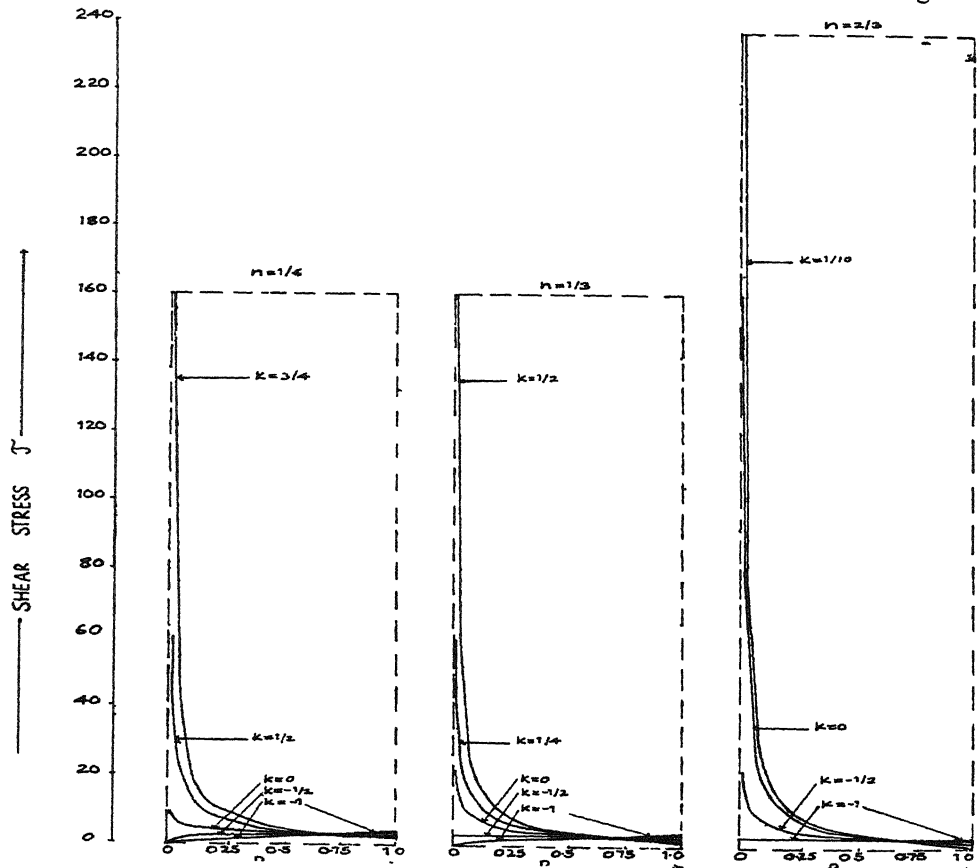


Fig. 1—Variation of shear stress in a non-homogeneous ( $\mu = \mu_0 r^{-2}$ ) cylinder under torsion

cylinder for the combinations  $n = 1/3$ ,  $k = -1/2$  and  $n = 2/3$ ,  $k = -1$ . This may provide a choice to the designer in selecting an appropriate material for the manufacture of cylindrical components.

Numerical calculations reveal that the shear stress ratio reduces to zero for the homogeneous material ( $k=0$ ) with  $n=2$ , as the torque  $M$  required in this case, theoretically becomes infinitely large, and the stress appears to be negative for  $k>0$  and  $n \geq 2$ . More realistic knowledge regarding the effects of non-homogeneity on the creep stresses of cylinders of various materials, subjected to torsion can be obtained from the numerical discussion of eqn. (22). For example, taking Poisson's ratio  $\nu_0 = 1/3$ , the value of  $t$  from eqn. (22) comes out to be unity and integrals may be evaluated by Simpson's rule for suitable values of  $k$ ,  $n$  etc.

Thus, the effects of non-homogeneity of the assumed form on the torsion of cylinder in the theory of creep are prominent. The presence of non-homogeneity  $k<0$ , reduces magnitude of the shear stress significantly and may be beneficial from a design point of view, while for  $k>0$ , the stress increases promptly at the centre of the incompressible cylinder and may not be useful with higher values of  $k$  and  $n$ .

### References

- 1 Saint-Venant, B de (1855) *Memories de l'academic des sciences des savants etrangers*, **14** . 233.
2. Love, A E H. (1944) *A Treatise on the Mathematical Theory of Elasticity*, 4<sup>th</sup> Ed. Dover, New York
3. Sokolnikoff, I S (1956) *Mathematical Theory of Elasticity*, 2<sup>nd</sup> Ed , Mc Graw Hill, New York.
- 4 Chakaraborty, J (1987) *Theory of Plasticity*, Mc Graw Hill, New York
5. Rabotnov, Y.N (1967) *Creep Problems in Structural Members*, North , and, London
6. Lee, Y.W. ( 1977) *Quart Appl Math*, **35** 410.
7. Cho, U.W & Findley, W.N. (1983) *Jr Appl Mech ASME*, **50** 580
8. Lau, J H. Jung, S.S & Lau, T T. (1984) *Jr Engg Gas Turb Power*, ASME, **106** . 79
- 9 Reissner, E. & Sagoci, H.F. (1944) *Jr Appl Phys* , **15** . 652
10. Erguven, M E. (1982) *Lett Appl Egg Sci* **20** . 675.
11. Chaudhuri, P.K & Datta, S (1989) *Jour Math Phy Sci* **23** . 351
12. Cowin, S.C. ( 1987) *Jr Appl Mech ASME*, **54** : 778
13. Bhatanagar, N.S., Kulkarni, P.S. & Arya, V K (1986) *Int J Non-Linear Mech.* **21** : 61.
14. Seth, B.R. (1966) *Int J Non-linear Mech.* **1** . 35.
15. Seth, B.R. (1964) *ZAMM* **44** : 229.

- 16 Gupta, S K & Rana, V D (1989) *Jour Math Phy Sci* **23** 71
- 17 Shukla, R K (1997) *Ind J Pure Appl Math* **28** 277
- 18 Shukla, R K (1999) *Proc Nat Acad Sci India* **69(A)** 293
- 19 Gupta, S K Dharmani, R L & Rana, V D (1979) *Int J Non-linear Mech* **13** 303
- 20 Gupta, S K. & Rana, V D (1980) *ZAMM* **60** 549
- 21 Hulsurkar, S (1979) *Jour Math Phy Sci* **13** 209
- 22 Gupta, S K & Shukla (1993) *Ind J Pure Appl Math* **24** . 417.
- 23 Gupta, S K & Shukla, R K (1993) *Ind J Pure Appl Math* **27** . 487
- 24 Gupta, S K and Shukla, R K (1994) *Ind J Pure Appl Math* **25** 1089

# **Eigen value approach to a micropolar viscoelastic medium**

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## **Abstract**

The dynamic problem in micropolar viscoelastic medium has been investigated by employing eigenvalue approach after applying Laplace and Hankel transformations. An example of infinite space with concentrated force at the origin has been presented to illustrate the application of the approach. The integral transforms have been inverted by using a numerical technique to obtain the radial displacement, normal displacement, normal force stress, shear stress, couple stress and microrotation in the physical domain. The results for these quantities are given and illustrated graphically.

**(Keywords)** micropolar viscoelastic medium/eigen value/Hankel and Laplace transformation)

## **Introduction**

Modern engineering structures are often made up of materials possessing an internal structure. Polycrystalline materials, materials with fibrous or coarse grain structures come in this category. Classical elasticity is inadequate to represent the behaviour of such materials. The analysis of such materials require incorporating the theory of oriented media. For this reason, micropolar theories were developed by Eringen<sup>1-3</sup> for elastic solid, fluids and further for non-local polar fields and are now universally accepted. A micropolar continuum is a collection of interconnected particles in form of small rigid bodies undergoing both translational and rotational motions. Different authors<sup>4-13</sup> discussed different type of problems in micropolar elastic medium.

Eringen<sup>14</sup> extended the theory of micropolar elasticity to obtain linear constitutive theory for micropolar material possessing internal friction. A problem on micropolar

viscoelastic waves has been discussed by McCarthy and Eringen<sup>15</sup>. They discussed the propagation conditions and growth equations governing the propagation of waves in micropolar viscoelastic medium. Ciccio and Nappa<sup>16</sup> discussed a problem of Saint Venant's principles for micropolar viscoelastic bodies. Kumar *et al.*<sup>17</sup> studied Lamb's plane problem in a micropolar viscoelastic half-space with stretch. Recently, Kumar<sup>18</sup> discussed wave propagation in micropolar viscoelastic generalized thermoelastic solid. Most of the problems studied so far, in micropolar viscoelastic, involve the use of potential functions. However, the use of the eigen value approach has the advantage of finding the solution of eqns in the coupled form directly, in the matrix notations, whereas the potential function approach requires decoupling of eqns. Yet, much work has not been done in micropolar viscoelastic solid using the eigen value approach. Mahalanabis and Manna<sup>19</sup> applied eigen-value approach of linear micropolar elasticity by arranging basic eqns of linear micropolar viscoelastic in the form of matrix differential eqn. Recently, Mahalanabis and Manna<sup>20</sup> discussed the problem of linear micropolar thermoelasticity by using eigen value approach.

In this paper, we consider a two dimensional axisymmetric problem in a homogeneous isotropic micropolar viscoelastic medium. The solutions were obtained by using eigen value approach after employing integral transformations technique. The integral transforms were inverted using a numerical approach.

### Basic Equations

Following Eringen<sup>14</sup> the constitutive relations and the field eqns in micropolar viscoelastic solid without body forces and body couples can be written as

$$t_{ij} = \lambda_l u_{k,k} \delta_{ij} + \mu_l (u_{i,j} + u_{j,i}) + K_l (u_{j,i} - \epsilon_{ijk} \phi_k), \quad (1)$$

$$m_{ij} = \alpha_1 \phi_{k,k} \delta_{ij} + \beta_1 \phi_{i,j} + \gamma_1 \phi_{j,i} \quad (2)$$

$$(\lambda_1 + 2\mu_1 + K_1) \Delta \Delta \vec{u} - (\mu_1 + K_1) \Delta \times \Delta \times \vec{u} + K_1 \Delta \times \vec{\phi} = \rho \frac{\partial^2 \vec{u}}{\partial t^2} \quad (3)$$

$$(\alpha_1 + \beta_1 + \gamma_1) \Delta \nabla \vec{\phi} + K_1 \Delta \times \vec{u} - 2K_1 \vec{\phi} = \rho j \frac{\partial^2 \vec{\phi}}{\partial t^2} \quad (4)$$

where,

$$\lambda_1 = \lambda + \lambda_\nu \frac{\partial}{\partial t}, \quad \mu_1 = \mu + \mu_\nu \frac{\partial}{\partial t}, \quad K_1 = K + K_\nu \frac{\partial}{\partial t} \quad (5)$$

$$\alpha_1 = \alpha + \alpha_\nu \frac{\partial}{\partial t}, \quad \beta_1 = \beta + \beta_\nu \frac{\partial}{\partial t}, \quad \gamma_1 = \gamma + \gamma_\nu \frac{\partial}{\partial t} \quad (6)$$

where,  $\lambda, \mu, K, \alpha, \beta, \gamma, \lambda_\nu, \mu_\nu, K_\nu, \alpha_\nu, \beta_\nu, \gamma_\nu$  are material constants,  $\rho$  is the density,  $j$  is the micro inertia,  $\vec{u}$  is the displacement vector,  $\vec{\phi}$  is the microrotation vector,  $t_{ij}$  is the force stress tensor,  $m_{ij}$  is the couple stress tensor. The necessary and sufficient conditions for the internal energy to be non-negative, as given by Eringen<sup>14</sup> are

$$\begin{aligned} 0 \leq 3\lambda + 2\mu + K, & \quad 0 \leq \mu, & \quad 0 \leq K \\ 0 \leq 3\alpha + 2\gamma & \quad -\gamma \leq \beta \leq \gamma, & \quad 0 \leq \gamma \end{aligned} \quad (7)$$

and

$$\begin{aligned} 0 \leq 3\lambda_\nu + 2\mu_\nu + K, & \quad 0 \leq \mu, & \quad 0 \leq K \\ 0 \leq 3\alpha_\nu + 2\gamma_\nu & \quad -\gamma_\nu \leq \beta_\nu \leq \gamma_\nu, & \quad 0 \leq \gamma_\nu \end{aligned} \quad (7)$$

### Formulation and Solution

We consider a homogeneous, isotropic micropolar viscoelastic medium of infinite extent with cylindrical polar co-ordinate system  $(r, \theta, z)$ . To analyze displacement and stresses at the interior of the medium due to concentrated load, the continuum is divided into two half-space defined by

$$\bullet \text{Half-space I: } |r| < \infty \quad -\infty < z \leq 0,$$

$$\bullet \text{Half-space II: } |r| < \infty \quad 0 \leq z < \infty.$$

As we are discussing an axi-symmetric problem so we take

$$\vec{u} = (u_r, 0, u_z), \quad \vec{\phi} = (0, \phi_\theta, 0) \quad (9)$$

We define dimensionless quantities as

$$\begin{aligned} r' &= \frac{r}{h}, \quad z' = \frac{z}{h}, & u'_r &= \frac{\rho h \omega^{*2} u_r}{\mu_1}, & u'_z &= \frac{\rho h \omega^{*2} u_z}{\mu_1}, \\ \phi'_\theta &= \frac{\rho h^2 \omega^{*2} u_\theta}{\mu_1} \phi_\theta, & t' &= \frac{\mu}{\rho h^2 \omega^*} t, & t'_z &= \frac{1}{K_1} t_z, \\ t'_z &= \frac{1}{K_1} t_z, & m'_{z\theta} &= \frac{1}{K_1} m_{z\theta}, & \omega^{*2} &= \frac{K_1}{\rho j} \end{aligned} \quad (10)$$

where  $h$  is a constant having dimension of length.

Due to axi symmetry about  $z$ -axis the quantities are independent of  $\theta$ . With these considerations and using (9) and (10) in eqns. (3) and (4) we obtain : (on suppressing the primes).

$$\left[ \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} - \frac{1}{r^2} \right] u_r + (1 - a^2) \frac{\partial^2 u_z}{\partial r \partial z} + a^2 \frac{\partial^2 u_r}{\partial z^2} - s_4^* \frac{\partial \phi_\theta}{\partial z} = \frac{1}{(s_1 + s_2)} \frac{\partial^2 u_r}{\partial t^2}, \quad (11)$$

$$\frac{\partial^2 u_z}{\partial z^2} + (1 - a^2) \left[ \frac{\partial^2 u_r}{\partial r \partial z} + \frac{1}{r} \frac{\partial u_r}{\partial z} \right] + a^2 \left[ \frac{\partial^2 u_z}{\partial r^2} + \frac{1}{r} \frac{\partial u_z}{\partial r} \right] + s_4^* \frac{1}{r} \frac{\partial}{\partial r} (r \phi_\theta) = \frac{1}{(s_1 + s_2)} \frac{\partial^2 u_z}{\partial t^2}, \quad (12)$$

$$s_4 \left[ \frac{\partial^2 \phi_\theta}{\partial r^2} + \frac{1}{r} \frac{\partial \phi_\theta}{\partial r} + \frac{\partial^2 \phi_\theta}{\partial z^2} - \frac{\phi_\theta}{r^2} \right] - \frac{h^2 s_3 \phi_\theta}{j} + \frac{2h^2 s_3}{j} \left( \frac{\partial u_r}{\partial z} - \frac{\partial u_z}{\partial r} \right) = \frac{\partial^2 \phi_\theta}{\partial t^2} \quad (13)$$

where

$$s_1 = \frac{\rho h^2 (\lambda_I + \mu_I) \omega^2}{\mu_I^2}, \quad s_2 = \frac{\rho h^2 (\mu_I + K_I) \omega^2}{\mu_I^2}, \quad s_3 = \frac{\rho h^2 K_I \omega^2}{\mu_I^2},$$

$$s_4 = \frac{\gamma_I \rho h^2 \omega^2}{j \mu_I^2}, \quad a^2 = \frac{s_2}{s_1 + s_2}, \quad s_4^* = \frac{s_3}{s_1 + s_2}.$$

Applying Laplace transform w.r.t. time variable 't' defined by

$$\{\bar{u}_r(r, z, p), \bar{u}_z(r, z, p), \bar{\phi}_\theta(r, z, p) = \int_0^\infty \{u_r(r, z, t), u_z(r, z, t), \phi_\theta(r, z, t)\} e^{-pt} dt \quad (14)$$

and then Hankel transform w.r.t. space variable 'r' defined by

$$\{\tilde{u}_r(\xi, z, p), \tilde{\phi}_\theta(\xi, z, p)\} = \int_0^\infty \{u_r(r, z, p)(z, r, p), u_z(r, z, p), \bar{\phi}_\theta(r, z, p)\} r J_0(\xi r) dr, \quad (15)$$

$$\bar{u}_r(\xi, z, p) = \int_0^\infty \bar{u}_r(r, z, p) r J_1(\xi r) dr, \quad (16)$$

on eqns (11) – (13), we obtain

$$\tilde{u}_r'' = \frac{1}{a^2} \left[ \xi^2 + \frac{p^2}{s_1 + s_2} \right] \bar{u}_r + \frac{(1-a^2)\xi}{a^2} \tilde{u}_z' + \frac{s_4^*}{a^2} \tilde{\Phi}_\theta, \quad (17)$$

$$\tilde{u}_z'' = \left[ a^2 \xi^2 + \frac{p^2}{s_1 + s_2} \right] \bar{u}_z - (1-a^2) \xi \tilde{u}_r' - \xi s_4^* \tilde{\Phi}_\theta', \quad (18)$$

and

$$\tilde{\Phi}_\theta'' = -\frac{K_I h^2}{\gamma_I} \tilde{u}_r' - \frac{K_I h^2 \xi}{\gamma_I} \tilde{u}_z' + \left[ \xi^2 + \frac{2K_I h^2}{\gamma_I} + \frac{p^2}{s_4} \right] \tilde{\Phi}_\theta, \quad (19)$$

The system of eqns. (17) – (19) can be written as

$$\frac{d}{dz} W(\xi, z, p) = A(\xi, p) W(\xi, z, p), \quad (20)$$

where,

$$W = \begin{bmatrix} U \\ U' \end{bmatrix}, \quad A = \begin{bmatrix} 0 & I \\ A_2 & A_1 \end{bmatrix}, \quad U = \begin{bmatrix} \tilde{u}_r \\ \tilde{u}_z \\ \tilde{\Phi}_\theta \end{bmatrix}$$

$$O = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad I = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$A_1 = \begin{bmatrix} 0 & \frac{(1-a^2)\xi}{a^2} & \frac{s_4^*}{a^2} \\ -(1-a^2)\xi & 0 & 0 \\ -\frac{K_I h^2}{\gamma_I} & 0 & 0 \end{bmatrix}$$

$$A_1 = \begin{bmatrix} \frac{1}{a^2} \left( \xi^2 + \frac{p^2}{(s_1 + s_2)} \right) & 0 & 0 \\ 0 & a^2 \xi + \frac{p^2}{(s_1 + s_2)} & -s_4^* \xi \\ 0 & -\frac{K_1 \xi h^2}{\gamma_1} & \xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \end{bmatrix} \quad (21)$$

To solve eqn. (20), we take

$$W(\xi, z, p) = X(\xi, p) e^{qz} \quad (22)$$

so that

$$A(\xi, p) W(\xi, z, p) = q W(\xi, z, p) \quad (23)$$

which leads to eigen value problem. The characteristic eqn. corresponding to the matrix  $A$  is given by

$$\det [A - qI] = 0 \quad (24)$$

which on expansion provides us

$$q^6 - \lambda_1 q^4 + \lambda_2 q^2 - \lambda_3 = 0$$

where

$$\lambda_1 = \left( 1 + \frac{1}{a^2} \right) \frac{p^2}{(s_1 + s_2)} + \left[ 3\xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} - \frac{K_1 h^2 s_4^*}{\gamma_1 a^2} \right] \quad (26)$$

$$\lambda_2 = \left[ \xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \right] \left[ \frac{p^2}{(s_1 + s_2)} + \left( 1 + \frac{1}{a^2} \right) 2\xi^2 \right]$$

$$-s_4^* \frac{K_1 h^2}{\gamma_1 a^2} \left[ 2\xi^2 + \frac{p^2}{(s_1 + s_2)} \right] + \frac{1}{a^2} \left[ \xi^2 + \frac{p^2}{(s_1 + s_2)} \right] \left[ a^2 \xi^2 + \frac{p^2}{(s_1 + s_2)} \right] \quad (27)$$

and

$$\lambda_3 = \frac{1}{a^2} \left[ \xi^2 + \frac{p^2}{(s_1 + s_2)} \right] \left[ a^2 \xi^2 + \frac{p^2}{(s_1 + s_2)} \right] \left[ \xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \right] - \frac{1}{\gamma_1 a^2} \left[ \xi^2 + \frac{p^2}{(s_1 + s_2)} \right] s_4^* K_1 h^2 \xi^2.$$

The roots of eqn. (25) are  $\pm q_i, i = 1, 2, 3$ .

The eigen value of the matrix  $A$  are the roots of eqn. (25). We assume that real part of  $q_i$  are positive. The vector  $X(\xi, p)$  corresponding to the eigen values  $q_i$  can be determined by solving the homogeneous eqn.

$$[A - qI] X(\xi, p) = 0 \quad (29)$$

The set of eigen vectors  $X_i(\xi, p), (i = 1, 2, 3, 4, 5, 6)$  may be obtained as

$$X_i(\xi, p) = \begin{bmatrix} X_{i1}(\xi, p) \\ X_{i2}(\xi, p) \end{bmatrix} \quad (30)$$

where,

$$X_{i1}(\xi, p) = \begin{bmatrix} a_i q_i \\ b_i \\ -\xi \end{bmatrix}, \quad X_{i2}(\xi, p) = \begin{bmatrix} a_i q_i^2 \\ -b_i q_i \\ \xi q_i \end{bmatrix}, \quad q = q_i, i = 1, 2, 3 \quad (31)$$

$$X_{j1}(\xi, p) = \begin{bmatrix} -a_i q_i \\ b_i \\ -\xi \end{bmatrix}, \quad X_{j2}(\xi, p) = \begin{bmatrix} a_i q_i^2 \\ -b_i q_i \\ \xi q_i \end{bmatrix}, \quad j=i+3, \quad q_i = -q_i, \quad i=1, 2, 3 \quad (32)$$

$$a_i = \left[ \xi(a^2 - 1) \left\{ \left( \xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \right) - q_i^2 \right\} - \frac{K_1 \xi h^2 s_4^*}{\gamma_1} \right] / \Delta \quad (33)$$

$$b_i = \left[ \left( \xi^2 + \frac{p^2}{(s_1 + s_2)} \right) \left( \xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \right) + a^2 q_i^2 \left\{ q_i^2 - \left( \xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \right) \right. \right. \\ \left. \left. - \left( \xi^2 + \frac{p^2}{(s_1 + s_2)} \right) q_i^2 + \frac{K_1 s_4^* h^2 q_i^2}{\gamma_1} \right\} \right] / \Delta \quad (34)$$

$$\Delta = \frac{K_1 h^2}{\gamma_1} \left[ q_i^2 - \left( \xi^2 + \frac{p^2}{(s_1 + s_2)} \right) \right] \quad (35)$$

The solution of eqn. (20) is given by

$$W(\xi, z, p) = \sum_{i=1}^3 [B_i X_i(\xi, p) \exp(q_i z) + B_{i+3} X_{i+3}(\xi, p) \exp(-q_i z)]$$

where,  $B_i$  ( $i = 1, 2, 3, 4, 5, 6$ ) are arbitrary constants.

The eqn. (36) represents the solution of the general problem in the axisymmetric case of homogeneous isotropic, micropolar viscoelasticity by employing the eigen value approach and therefore can be applied to a broad class of problem in the domains of Laplace and Hankle transforms.

### Application

We consider an infinite micropolar viscoelastic space in which a concentrated force of magnitude  $F = \frac{-F_0 \delta(r) \delta(t)}{2\pi r}$  acting in the direction of the  $z$ -axis at the origin of the cylindrical co-ordinate system. The problem is axisymmetric w.r.t. the  $z$ -axis. The boundary conditions at the plane  $z = 0$  are given by

$$u_r(r, 0^+, t) - u_r(r, 0^-, t) = 0, \quad u_z(r, 0^+, t) - u_z(r, 0^-, t) = 0, \quad (37)$$

$$\phi_\theta(r, 0^+, t) - \phi_\theta(r, 0^-, t) = 0, \quad (38)$$

$$m_{z\theta}(r, 0^+, t) - m_{z\theta}(r, 0^-, t) = 0, \quad (39)$$

$$t_{zr}(r, 0^+, t) - t_{zr}(r, 0^-, t) = 0, \quad (40)$$

$$t_{zz}(r, 0^+, t) - t_{zz}(r, 0^-, t) = -\frac{F_0 \delta(r) \delta(t)}{2\pi r} \quad (41)$$

Applying the Laplace and Hankel transforms to eqn. (37)–(41),

we get

$$\tilde{u}_r(\xi, 0^+, p) - \tilde{u}_r(\xi, 0^-, p) = 0, \quad \tilde{u}_z(\xi, 0^+, p) - \tilde{u}_z(\xi, 0^-, p) = 0, \quad (42)$$

$$\tilde{\phi}_\theta(\xi, 0^+, p) - \tilde{\phi}_\theta(\xi, 0^-, p) = 0, \quad (43)$$

$$\tilde{m}_{z\theta}(\xi, 0^+, p) - \tilde{m}_{z\theta}(\xi, 0^-, p) = 0, \quad (44)$$

$$\tilde{t}_z(\xi, 0^+, p) - \tilde{t}_z(\xi, 0^-, p) = 0, \quad (45)$$

$$\tilde{t}_{zz}(\xi, 0^+, p) - \tilde{t}_{zz}(\xi, 0^-, p) = -\frac{F_o}{2\pi}, \quad (46)$$

The transformed displacements, microrotation, couple stress and stresses are given for  $z \geq 0$  by

$$\tilde{u}_r(\xi, z, p) = -[a_1 q_1 B_4 \exp(-q_1 z) + a_2 q_2 B_5 \exp(-q_2 z) + a_3 q_3 B_6 \exp(-q_3 z)], \quad (47)$$

$$\tilde{u}_z(\xi, z, p) = b_1 B_4 \exp(-q_1 z) + b_2 B_5 \exp(-q_2 z) + b_3 B_6 \exp(-q_3 z) \quad (48)$$

$$\tilde{\phi}_\theta(\xi, z, p) = -\xi[B_4 \exp(-q_1 z) + B_5 \exp(-q_2 z) + B_6 \exp(-q_3 z)], \quad (49)$$

$$\tilde{m}_{z\theta}(\xi, z, p) = s_7 \xi[q_1 B_4 \exp(-q_1 z) + q_2 B_5 \exp(-q_2 z) + q_3 B_6 \exp(-q_3 z)], \quad (50)$$

$$\begin{aligned} \tilde{t}_r(\xi, z, p) = & (a_1 q_1^2 s_8 - \xi b_1 s_9 + \xi s_{10}) B_4 \exp(-q_1 z) \\ & + (a_2 q_2^2 s_8 - \xi b_2 s_9 + \xi s_{10}) B_5 \exp(-q_2 z) \\ & + (a_3 q_3^2 s_8 - \xi b_3 s_9 + \xi s_{10}) B_6 \exp(-q_3 z) \end{aligned} \quad (51)$$

$$\begin{aligned} \tilde{t}_{zz}(\xi, z, p) = & -[q_1 (b_1 s_6 + \xi a_1 s_5) B_4 \exp(-q_1 z) + q_2 (b_2 s_6 + \xi a_2 s_5) B_5 \exp(-q_2 z) \\ & + q_3 (b_3 s_6 + \xi a_3 s_5) B_6 \exp(-q_3 z)], \end{aligned} \quad (52)$$

and for  $z \leq 0$  by

$$\tilde{u}_r(\xi, z, p) = a_1 q_1 B_1 \exp(q_1 z) + a_2 q_2 B_2 \exp(q_2 z) + a_3 q_3 B_3 \exp(q_3 z), \quad (53)$$

$$\tilde{u}_z(\xi, z, p) = b_1 B_1 \exp(q_1 z) + b_2 B_2 \exp(q_2 z) + b_3 B_3 \exp(q_3 z) \quad (54)$$

$$\tilde{\phi}_\theta(\xi, z, p) = -\xi[B_1 \exp(q_1 z) + B_2 \exp(q_2 z) + B_3 \exp(q_3 z)], \quad (55)$$

$$\tilde{m}_{z\theta}(\xi, z, p) = -s_7 \xi[q_1 B_1 \exp(q_1 z) + q_2 B_2 \exp(q_2 z) + q_3 B_3 \exp(q_3 z)], \quad (56)$$

$$\begin{aligned} \tilde{t}_{xz}(\xi, z, p) = & (a_1 q_1^2 s_8 - \xi b_1 s_9 + \xi s_{10}) B_1 \exp(q_1 z) + (a_2 q_2^2 s_8 - \xi b_2 s_9 + \xi s_{10}) B_2 \exp(q_2 z) + \\ & (a_3 q_3^2 s_8 - \xi b_3 s_9 + \xi s_{10}) B_3 \exp(q_3 z) \end{aligned} \quad (57)$$

$$\begin{aligned} \tilde{t}_{zz}(\xi, z, p) = & q_1 (b_1 s_6 + \xi a_1 s_5) B_1 \exp(q_1 z) + q_2 (b_2 s_6 + \xi a_2 s_5) B_2 \exp(q_2 z) + q_3 (b_3 s_6 + \\ & \xi a_3 s_5) B_3 \exp(q_3 z), \end{aligned} \quad (58)$$

where,

$$\begin{aligned} s_5 &= \frac{\lambda_1 \mu_1}{\rho K_1 h^2 \omega^2}, & s_6 &= \frac{(\lambda_1 + 2\mu_1 + K_1) \mu_1}{\rho K_1 h^2 \omega^2}, & s_7 &= \frac{\gamma_1 \mu_1}{\rho K_1 h^4 \omega^2}, \\ s_8 &= \frac{(\mu_1 + K_1) \mu_1}{\rho K_1 h^2 \omega^2}, & s_9 &= \frac{\mu_1^2}{\rho K_1 h^2 \omega^2}, & s_{10} &= \frac{\mu_1}{\rho h^2 \omega^2} \end{aligned}$$

Using conditions (42)–(46) in eqns. (47)–(48), we obtain

$$a_1 q_1 (B_1 + B_4) + a_2 q_2 (B_2 + B_5) + a_3 q_3 (B_3 + B_6) = 0, \quad (59)$$

$$(B_1 - B_4) + (B_2 - B_5) + (B_3 - B_6) = 0, \quad (60)$$

$$b_1 (B_1 - B_4) + b_2 (B_2 - B_5) + b_3 (B_3 - B_6) = 0 \quad (61)$$

$$q_1 (B_1 + B_4) + q_2 (B_2 + B_5) + q_3 (B_3 + B_6) = 0 \quad (62)$$

$$[a_1 q_1^2 s_8 - \xi b_1 s_9 + \xi s_{10}] (B_1 - B_4) + [a_2 q_2^2 s_8 - \xi b_2 s_9 + \xi s_{10}] (B_2 - B_5)$$

$$+ (a_3 q_3^2 s_8 - \xi b_3 s_9 + \xi s_{10}) (B_3 - B_6) = 0 \quad (63)$$

$$q_1 (b_1 s_6 + \xi a_1 s_5) (B_1 + B_4) + q_2 (b_2 s_6 + \xi a_2 s_5) (B_2 + B_5) \\ + q_3 (b_3 s_6 + \xi a_3 s_5) (B_3 + B_6) = \frac{F_o}{2\pi} \quad (64)$$

Solving system of eqns. (59) – (60), we obtain

$$B_1 = B_4 \frac{F_o (a_3 - a_2)}{4\pi q_1 \Delta_1}, \quad (65)$$

$$B_5 = B_5 \frac{F_o (a_1 - a_3)}{4\pi q_2 \Delta_1}, \quad (66)$$

$$B_3 = B_6 \frac{F_o (a_2 - a_1)}{4\pi q_3 \Delta_1}, \quad (67)$$

where

$$\Delta_1 = s_6 [(a_2 b_3 - a_3 b_2) + (a_3 b_1 - a_1 b_3) + (a_1 b_2 - a_2 b_1)].$$

Thus the components  $\tilde{u}_r$ ,  $\tilde{u}_z$ ,  $\tilde{\phi}_\theta$ ,  $\tilde{m}_{z\theta}$ ,  $\tilde{t}_{rz}$ , and  $\tilde{t}_{zz}$  have been determined in the transform domain and these enable us to find the displacements, microrotation, couple stress and forces stress.

### Inversion of Transforms

The transformed displacements and stresses are functions of  $z$ , the parameters of Laplace and Hankel transforms  $p$  and  $\xi$  respectively, and hence are of the form  $f(\xi, z, p)$  in the physical domain, first we invert the Hankel transform using

$$\bar{f}(r, z, p) = \int_0^\infty \xi \bar{f}(\xi, z, p) J_n(\xi r) d\xi$$

Thus, expression (68) gives us the Laplace  $\bar{f}(r, z, p)$  of the function  $f(r, z, t)$ . We invert the Laplace transform by using the inversion technique as used in Kumar and Choudhary<sup>21</sup>

### Numerical Results and Discussion

Following Gauthier<sup>22</sup>, we take the following values of relevant parameters for the case of aluminum epoxy composite as

$$\begin{aligned} \rho &= 2.19 \text{ g/cm}^3, & \lambda &= 7.59 \times 10^{10} \text{ dyne/cm}^2, \\ \mu &= 1.89 \times 10^{10} \text{ dyne/cm}^2, & K &= 0.0149 \times 10^{10} \text{ dyne/cm}^2, \\ \gamma &= 0.0268 \times 10^{10} \text{ dyne}, & j &= .00196 \text{ cm}^2, \end{aligned}$$

For a particular model of micropolar viscoelastic solid the relevant parameters are expressed as

$$\chi = \chi (1 + iQ_i^{-1}) \quad i = 1, 2, 3, 4 \text{ for } \chi = \lambda, \mu, K, \gamma \text{ respectively}$$

where,

$$Q_1 = 0.05, \quad Q_2 = 0.01 \quad Q_3 = 0.015 \quad Q_4 = 0.1.$$

The comparison of values of dimensionless normal displacement  $U_z [(2\pi u_z/F_0)]$  and couple stress  $M_{z\theta} [(2\pi M_{z\theta}/F_0)]$  for micropolar elastic solid (ME) and micropolar viscoelastic solid (MVE) have been studied. The computations were carried out for two values of dimensionless time 0.05 and 0.10 and for  $h = 1$  at  $z = 1.0$  in the range  $0 \leq r \leq 10$ . The solid lines [—] in graphs represent the variations for time 0.05 and the dashed [----] represent the variations for time 0.10. For both the times, solid or dashed lines with center symbols represents the variations for ME, whereas without center symbols are for MVE.

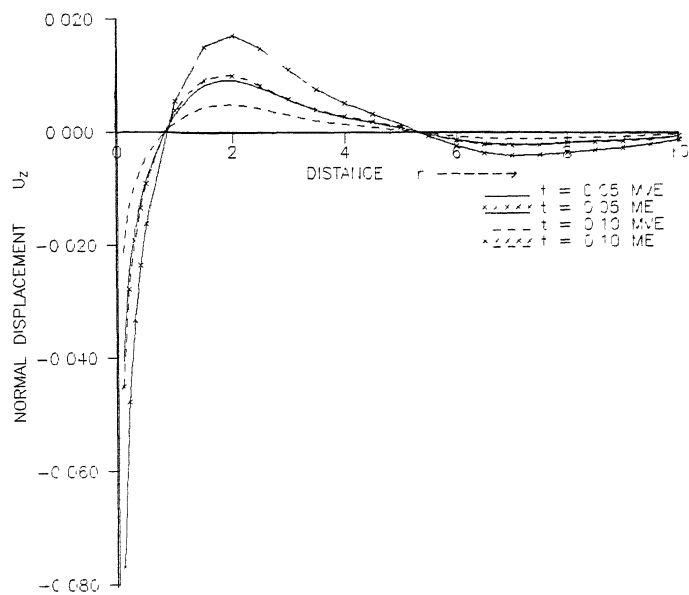


Fig. 1— Variations of normal displacement  $U_z(r,1)(=u_z2\pi/F_0)$  with distance  $r$

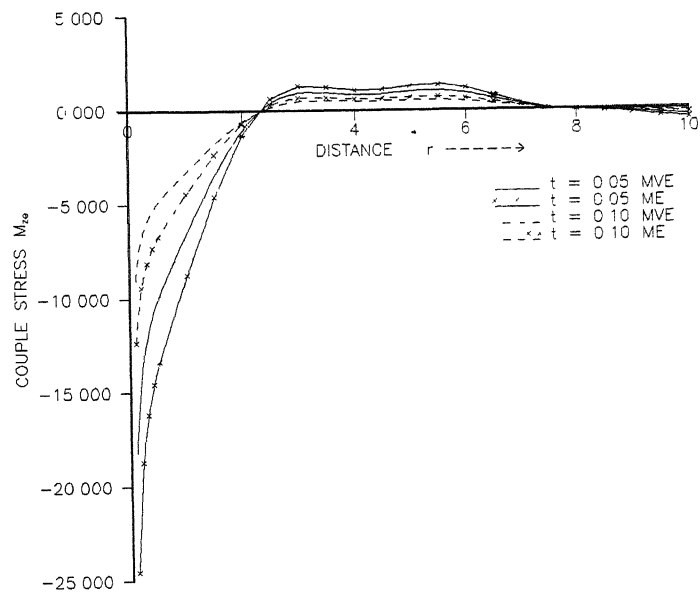


Fig. 2— Variations of couple stress  $M_{x\theta}(r,1)(=m_{x\theta}2\pi/F_0)$  with distance  $r$ .

Fig. 1 shows the variations of normal displacement  $U_z$  with  $r$ . In the range  $0 \leq r \leq 1$  and  $5.5 \leq r \leq 10$  the values of  $U_z$  for time 0.50 are less in comparison with those for time 0.10 whereas in the range  $1 \leq r \leq 5.5$  the time 0.05 are more than for time 0.10 for both MVE and ME. For fixed time 0.05 the values of  $U_z$  for MVE are more than those for ME in ranges  $0 \leq r \leq 1$  and  $5.5 \leq r \leq 10$  and less in the range  $1 \leq r \leq 5.5$ . The similar trends for time 0.10 have been shown.

Fig. 2 shows the variations of couple stress  $M_{z\theta}$  with  $r$ . The values of  $M_{z\theta}$  have been taken by multiplying their original values with  $10^3$ . In the ranges  $(0 \leq r \leq 2)$  and  $7 \leq r \leq 9$  the values of  $M_{z\theta}$  for time 0.05 are less than the values for time 0.10 and in the ranges  $2 \leq r \leq 7$  and  $9 \leq r \leq 10$  the values for time 0.05 are more than those for time 0.10 for both MVE and ME. For fixed time 0.05 the values of  $M_{z\theta}$  for MVE are more than those for ME in the ranges  $0 \leq r \leq 2$  and  $(7 \leq r \leq 10)$  and less for ME in the range  $2 \leq r \leq 7$ . The similar trends for time 0.10 have been shown.

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### References

1. Eringen, A C (1996) *J Math Mech* **15** . 909.
2. Eringen, A.C (1996) *J Math Mech* **16** . 1.
3. Eringen, A C (1976) *Not-local polar field theories. In Continuum Physics* (Edited by A.C Eringen), Vol IV, Academic press, New York, p 205
4. Cheng, Z.-Q. & He, L -H (1997) *Int J Engng Sci* **33** . 359
5. Cheng, Z.-Q. & He, L -H. (1997) *Int J Engng Sci* **35** 659
6. Eringen, A.C. & Suhubi, E S (1964) *Int J. Engng Sci* **2** . 189
7. Eringen, A.C. (1968) *Theory of Micropolar Elasticity in Fracture*, Vol II, Academic press p 621
8. Kumar, R & Singh, B. (2000) *Indian J Pure Appl Maths* **31** · 287
9. Nappa, L (1996) *Int J Engng. Sci* **34** : 1601.
10. Singh, B & Kumar, R. (1998) *Int J Engng Sci* **36** : 119
11. Singh, B. & Kumar, R. (1998) *Int J Engng. Sci* **36** : 865.
12. Suhubi, E.S. & Eringen, A.C. (1964) *Int J Engng. Sci.* **2** . 389.
13. Tomar, S K. & Kumar, R (1999) *Proc. Ind Acad Sci (Math Sci)*, **189** · 425

- 14 Eringen, A C (1967) *Int J Engng Sci* **5** 191
- 15 McCarethy, M F & Eringen, A C (1969) *Int J Engng Sci* **7** 447
- 16 Ciccio, S De, & Nappa, L (1998) *Int J Engng Sci* **36** 883
- 17 Kumar, R , Gogna, M L & Lokeshnath Debnath (1990) *Int J Math & Sci* **132** 363
- 18 Kumar, R (2000) *Int J Engng Sci* **38** 1377
- 19 Mahalabanbis, R K & Manna, J (1989) *Indian J Pure Appl Math* **20** 1237
- 20 Mahalabanbis, R K & Manna, J (1997) *J Indian Acad Math* **19** 69
- 21 Kumar, R & Choudhary, S (2001) *Proc Indian Acad Sci (Earth Plant Sci)* **110** 215
- 22 Gautheri, R D (1982) In *Experimental Investigations on Micropolar Media*, ed O Brulin and R K T Heseish, World Scientific, Singapore



## **Kelvin-Helmholtz instability of two viscous superposed conducting fluids**

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### **Abstract**

The Kelvin-Helmholtz instability of two superposed viscous conducting fluids in a uniform vertical magnetic field is discussed in the presence of effects of surface tension and permeability of porous medium. The dispersion relation has been derived through normal mode technique and solved numerically. The streaming velocity is found to have a destabilizing influence while viscosity, surface tension and permeability of the medium have all stabilizing influence on the growth rate of unstable mode of disturbance.

(**Keywords** Kelvin-Helmholtz instability/surface tension/ viscosity/porous medium)

### **Introduction**

The problem of the Kelvin-Helmholtz discontinuity between two superposed fluids is of prime importance in various astrophysical, geophysical and laboratory situations. The Kelvin-Helmholtz discontinuity arises when air is blown over mercury or when highly ionized hot plasma is surrounded by a slightly cold gas or when a meteor enters the earth's atmosphere. Chandrasekhar<sup>1</sup> has given a detailed account of the various investigations of this problem as investigated by different researchers for incompressible fluids. For the case of a low -  $\beta$  magnetized plasma in the presence of effects of compressibility, D' Angelo<sup>2</sup> found that a velocity difference between adjacent field-aligned flows, on the order of the ion-acoustic speed  $c_s$ , is sufficient for instability. The results of his calculations were in agreement with experimental findings in a Q-machine (D' Angelo and von Geoler<sup>3</sup>). Gerwin<sup>4</sup> has examined the stability problem of the non-conducting streaming gas flowing over an incompressible conducting fluid. Kalra, Lister and Hosking<sup>5</sup> have investigated Kelvin-Helmholtz instability of superposed fluids in the presence of the effects of magnetic resistivity while Bhatia and Steiner<sup>6</sup> have analysed this problem for partially ionized plasmas. Shivamoggi<sup>7</sup> has studied the effect of finite magnetic resistivity on the Kelvin-Helmholtz instability of superposed plasmas. Sengar<sup>8</sup> has analysed the stability of

superposed gravitating streams in a uniform vertical magnetic field in the presence of effects of magnetic resistivity. Mehta and Bhatia<sup>9</sup> investigated Kelvin-Helmholtz instability of two viscous, superposed, rotating and conducting fluids. Singh and Khare<sup>10</sup> have investigated the stability of two semi-infinite homogeneous gravitating streams of infinite conductivity under uniform horizontal magnetic field and uniform rotation. Eldabe and Hassan<sup>11</sup> have examined the effects of surface tension and finite magnetic resistivity on the Kelvin-Helmholtz instability of superposed fluids in a horizontal magnetic field. Bhatia and Hazarika<sup>12</sup> discussed this stability problem for superposed viscous gravitating fluids. The importance of the Kelvin-Helmholtz problem has been demonstrated recently by Benjamin and Bridges<sup>13-14</sup> who have given an excellent reappraisal of the classic Kelvin-Helmholtz problem in hydrodynamics. They have shown that the problem admits of a canonical Hamiltonian formulation and obtained several new results. More recently Sharma and Kumar<sup>15</sup> have studied the Rayleigh-Taylor instability of two superposed conducting Walter's B' elasticoviscous fluids in hydromagnetics while Allah<sup>16</sup> has investigated the effects of magnetic field and heat and mass transfer on the Kelvin-Helmholtz instability of superposed fluids.

The flow through porous medium has been of considerable importance in recent years particularly among geophysical fluid dynamicists and petroleum engineers. The physical properties of the comets, meteorites and interplanetary dust strongly suggest the significance of the effects of porosity in astrophysical context (Mc Donnell<sup>17</sup>). Several authors<sup>18-22</sup> have investigated the effects of permeability of the porous medium on different stability problems.

The aim of this paper is to study the Kelvin-Helmholtz discontinuity between two viscous conducting fluids in a uniform vertical magnetic field through a porous medium in the presence of the effects of surface tension.

### Perturbation Equations

Consider the motion of an incompressible, infinitely conducting viscous fluid of variable viscosity  $\mu_0(z)$  through porous medium having a streaming velocity  $U$  along  $x$ -direction. The magnetic field is taken to be uniform and vertical. If we denote by  $\vec{u}$  ( $u, v, w$ ),  $\vec{h}$  ( $h_x, h_y, h_z$ ),  $\delta\rho$  and  $\delta p$ , the perturbations in Darcian velocity, magnetic field  $\vec{H}$ , density  $\rho$  and pressure  $p$  respectively, then the linearized perturbation equations appropriate to the problem are

$$\frac{\rho}{\epsilon} \frac{\partial \vec{u}}{\partial t} + \frac{\rho}{\epsilon} (\vec{U} \cdot \nabla) \vec{u} = -\nabla \delta p + \vec{g} \delta \rho + (\nabla \times \vec{h}) \times \vec{H} + \frac{\mu}{\epsilon} \nabla^2 \vec{u}$$

$$-\frac{\mu}{\lambda}\vec{u} + \Sigma \left[ T_s \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \delta z_s \right] \delta(z - z_s) \quad (1)$$

$$\epsilon \frac{\partial \vec{h}}{\partial t} + (\vec{U} \cdot \nabla) \vec{h} = (\vec{H} \cdot \nabla) \vec{u} \quad (2)$$

$$\epsilon \frac{\partial}{\partial t} \delta \rho + (\vec{U} \cdot \nabla) \delta \rho + (\vec{u} \cdot \nabla) \rho = 0 \quad (3)$$

$$\epsilon \frac{\partial}{\partial t} \delta z_s + w_s \quad (4)$$

$$\nabla \cdot \vec{u} = 0 \quad (5)$$

$$\nabla \cdot \vec{h} = 0 \quad (6)$$

As stated above, we take streaming velocity  $\vec{U} = (U, 0, 0)$  and magnetic field  $\vec{H} = (0, 0, H_0)$ . Here,  $T$ ,  $\mu$  and  $\vec{g} = (0, 0, -g)$  denote surface tension, coefficient of viscosity and acceleration due to gravity respectively. In equation (1),  $\delta(z - z_s)$  denotes Dirac's  $\delta$  function,  $\lambda$  denotes permeability of porous medium and  $\epsilon$  is the medium porosity.

Analyzing the disturbances in terms of normal modes, we assume that the perturbed quantities have dependence on space coordinates  $x$ ,  $z$  and time  $t$  of the form

$$F(z) \exp(ik_x x + nt) \quad (7)$$

where  $F(z)$  is some function of  $z$ ,  $k_x$  is the wave number along  $x$ -direction and  $n$  (may be complex) is the frequency of the harmonic disturbance.

Using equation (7) in equations (1) to (6), we get

$$\frac{\rho}{\epsilon} (n + ik_x U) u = -ik_x \delta p + H_0 D h_x - H_0 i k_x h_z + \frac{\mu}{\epsilon} (D^2 - k^2) u - \frac{\mu}{\lambda} u \quad (8)$$

$$\frac{\rho}{\epsilon}(n + ik_x U) v = H_0 D h_y + \frac{\mu}{\epsilon} (D^2 - k_x^2) v - \frac{\mu}{\lambda} v \quad (9)$$

$$\frac{\rho}{\epsilon}(n + ik_x U) w = -D \delta \rho - g \delta \rho + \frac{\mu}{\epsilon} (D^2 - k_x^2) w - \frac{\mu}{\lambda} w - \frac{k_x^2 T}{n \epsilon} \delta(z - z_s) w \quad (10)$$

$$\epsilon (n + ik_x U) h_x = H_0 D u \quad (11)$$

$$\epsilon (n + ik_x U) h_y = H_0 D v \quad (12)$$

$$\epsilon (n + ik_x U) h_z = H_0 D w \quad (13)$$

$$(n + ik_x U) \delta \rho = -(D \rho) w \quad (14)$$

$$ik_x h_x + D h_z = 0 \quad (15)$$

$$ik_x u + D w = 0 \quad (16)$$

where

$$D = \frac{d}{dz}$$

Eliminating some of the variables from the above equations, we obtain an equation in  $w$  as

$$\begin{aligned} & \frac{n' \rho}{\epsilon} [k_x^2 \rho w - D(\rho D w)] - \frac{g k_x^2}{n' \epsilon} w + \frac{H_0^2}{n' \epsilon} (D^2 - k_x^2) D^2 w \\ & + \frac{\mu}{\epsilon} (D^2 - k_x^2)^2 w - \frac{\mu}{\lambda} (D^2 - k_x^2) w + \frac{k_x^4}{n' \epsilon} \delta(z - z_s) w = 0 \end{aligned} \quad (17)$$

where we have written  $n' = (n + ik_x U)$ .

### Two Superposed Streaming Fluids

We now consider the case when two superposed fluids of uniform viscosities  $\mu_1$  and  $\mu_2$ , uniform densities  $\rho_1$  and  $\rho_2$ , magnetic fields  $H_1$  and  $H_2$  and with streaming velocities  $U_1$  and  $U_2$  are separated by a horizontal boundary at the interface  $z = 0$ . Therefore, in both the regions  $z < 0$  and  $z > 0$  of constant densities, equation (17) becomes

$$(D^2 - k_x^2) (D^2 - M^2) w = 0 \quad (18)$$

where

$$M^2 = \frac{k_x^2 n' \nu}{n' \nu + V_A^2} \left( 1 + \frac{\epsilon}{\lambda k_x^2} + \frac{n'}{\nu k_x^2} \right) \quad (19)$$

In equation (19),  $\nu = \frac{\mu}{\rho}$  is the coefficient of kinematic viscosity while  $V_A^2 = \frac{H_0^2}{\rho}$  is the Alfvén velocity

Now, seeking the solutions of equation (18), which remain bounded in the two regions, we obtain

$$w_1 = A_1 n'_1 e^{k_x z} + B_1 n'_1 e^{M_1 z}; \quad z < 0 \quad (20)$$

$$w_2 = A_2 n'_2 e^{-k_x z} + B_2 n'_2 e^{-M_2 z}; \quad z > 0 \quad (21)$$

where  $A_1, A_2, B_1$  and  $B_2$  are constants of integration and  $M_1$  and  $M_2$  are square roots of equation (19) and

$$n'_1 = n + ik_x U_1; \quad n'_2 = n + ik_x U_2 \quad (22)$$

and

$$M_1^2 = \frac{k_x^2 n'_1 v_1}{n'_1 v_1 + V_1^2} \left[ 1 + \frac{\epsilon_1}{\lambda_1 k_x^2} + \frac{n'_1}{v_1 k_x^2} \right] \quad (23)$$

$$M_2^2 = \frac{k_x^2 n'_2 v_2}{n'_2 v_2 + V_2^2} \left[ 1 + \frac{\epsilon_2}{\lambda_2 k_x^2} + \frac{n'_2}{v_2 k_x^2} \right] \quad (24)$$

are the values of  $M_1$  and  $M_2$  for the two regions. Since  $n'$  is complex,  $M_2$  is therefore complex and consequently  $M_1$  and  $M_2$  are complex. In writing the solutions (20) and (21) it is assumed that  $M_1$  and  $M_2$  are so defined that their real parts are positive.

The above solutions must satisfy certain boundary conditions. These conditions require that at an interface  $z = 0$ ,

$$w, Dw \text{ and } \mu (D^2 + k_x^2) w \quad (25a, b, c)$$

must be continuous.

If we integrate equation (17) across the interface  $z = 0$ , we obtain another condition

$$\begin{aligned} & \left[ n'_2 \rho_2 Dw_2 - \mu_2 (D^2 - k_x^2) Dw_2 - \frac{H_2^2}{n'_2} (D^2 - k_x^2) Dw_2 + \frac{\mu_2 \epsilon}{\lambda} Dw_2 \right]_{z=0} \\ & - \left[ n'_1 \rho_1 Dw_1 - \mu_1 (D^2 - k_x^2) Dw_1 - \frac{H_1^2}{n'_1} (D^2 - k_x^2) Dw_1 + \frac{\mu_1 \epsilon}{\lambda} Dw_1 \right]_{z=0} \\ & = -k_x^2 \left\{ g \left( \frac{\rho_2}{n'_2} - \frac{\rho_1}{n'_1} \right) - k_x^2 T \right\} w_0 - 2 k_x^2 (\mu_2 - \mu_1) (Dw)_0 \end{aligned} \quad (26)$$

where  $w_0$  and  $(Dw)_0$  are the unique values of these quantities at  $z = 0$ . If we apply the conditions (25) and (26) to the solutions (20) and (21), we obtain

$$A_1 + B_1 = A_2 + B_2 \quad (27)$$

$$k_x A_1 + M_1 B_1 = -k_x A_2 - M_2 B_2 \quad (28)$$

$$\begin{aligned} & \mu_1 [2k_x^2 A_1 + (M_1^2 + k_x^2) B_1] \\ &= \mu_2 [2k_x^2 A_2 + (M_2^2 + k_x^2) B_2] \end{aligned} \quad (29)$$

$$\begin{aligned} & A_2 (-k_x \rho_2 n'_2) - \frac{H_2^2 k_x^2}{n'_2} M_2 B_2 + A_1 (-k_x \rho_1 n'_1) - \frac{H_1^2 k_x^2}{n'_1} M_1 B_1 \\ &= -\frac{k_x^2}{2} \left[ g \left( \frac{\rho_2}{n'_2} - \frac{\rho_1}{n'_1} \right) - k_x^2 T \right] (A_1 + B_1 + A_2 + B_2) \\ & - k_x^2 (\mu_2 - \mu_1) (k_x A_1 + M_1 B_1 - k_x A_2 - M_2 B_2) \end{aligned} \quad (30)$$

Eliminating the constants  $A_1, B_1, A_2$  and  $B_2$  from equations (27) to (30) and writing

$$R = \frac{gk_x}{2} \left[ \left( \frac{\alpha_2}{n'_2} - \frac{\alpha_1}{n'_1} \right) - \frac{k_x^2 T}{g(\rho_1 + \rho_2)} \right] \quad (31)$$

$$C = k_x^2 (\alpha_2 v_2 - \alpha_1 v_1), \quad \alpha_{1,2} = \frac{\rho_{1,2}}{\rho_1 + \rho_2} \quad (32)$$

we obtain the following characteristic equation

$$\begin{aligned} & (M_1 - k_x) \left[ 2k_x^2 (\alpha_1 v_1 - \alpha_2 v_2) \left\{ \frac{k_x V_2^2}{n'_2} M_2 + \frac{C}{k_x} (M_2 - k_x) - \alpha_2 n'_2 \right\} \right. \\ & \left. + \alpha_2 v_2 (M_2^2 - k_x^2) \{ \alpha_2 n'_2 + \alpha_1 n'_1 - 2R \} \right] \end{aligned}$$

$$\begin{aligned}
& -2k_x \left[ \alpha_1 v_1 (M_1^2 - k_x^2) \left\{ \frac{k_x V_2^2}{n_2'} M_2 + \frac{C}{k_x} (M_2 - k_x) - \alpha_2 n_2' \right\} \right. \\
& \quad \left. + \alpha_2 v_2 (M_2^2 - k_x^2) \left\{ \frac{k_x V_1^2}{n_1'} M_1 + \frac{C}{k_x} (M_1 - k_x) - \alpha_1 n_1' \right\} \right] \\
& -2k_x \left[ \alpha_1 v_1 (M_1^2 - k_x^2) \left\{ \frac{k_x V_2^2}{n_2'} M_2 + \frac{C}{k_x} (M_2 - k_x) - \alpha_2 n_2' \right\} \right. \\
& \quad \left. + \alpha_2 v_2 (M_2^2 - k_x^2) \left\{ \frac{k_x V_1^2}{n_1'} M_1 + \frac{C}{k_x} (M_1 - k_x) - \alpha_1 n_1' \right\} \right] \\
& + (M_2 - k_x) [\alpha_1 v_1 (M_1^2 - k_x^2) \{\alpha_2 n_2' + \alpha_1 n_1' - 2R\} \\
& - 2k_x^t (\alpha_1 v_1 - \alpha_2 v_2) \left\{ \frac{k_x V_1^2}{n_1'} M_1 + \frac{C}{k_x} (M_1 - k_x) - \alpha_1 n_1' \right\}] = 0 \quad (33)
\end{aligned}$$

wherein the subscript  $A$  on Alfvén velocity  $V_A$  has been dropped for convenience. The dispersion relation (33) is quite complex. We therefore, consider the case of two highly viscous and highly permeable fluids for then we can write

$$M_1 = k + \frac{\alpha_1 n_1' + \alpha_1 v_1 \frac{\epsilon_1}{\lambda_1} - \frac{k^2 V_1^2}{n_1'}}{2k \left[ \alpha_1 v_1 + \frac{V_1^2}{2n_1'} \right]} \quad (34)$$

$$M_2 = k + \frac{\alpha_2 n_2' + \alpha_2 v_2 \frac{\epsilon_2}{\lambda_2} - \frac{k^2 V_2^2}{n_2'}}{2k \left[ \alpha_2 v_2 + \frac{V_2^2}{2n_2'} \right]} \quad (35)$$

Now we consider the case of two streams, of equal Alfvén velocities and same kinematic viscosities and same permeabilities, flowing past each in opposite directions with equal velocities i.e.

$$\begin{aligned} V_1 = V_2 = V, \quad v_1 = v_2 = v, \quad U_1 = U, \quad U_2 = -U \\ \epsilon_1 = \epsilon_2 = \epsilon, \quad \lambda_1 = \lambda_2 = \lambda \end{aligned} \quad (36)$$

Now substituting the values of  $M_1$  and  $M_2$  from equations (34) and (35), the dispersion relation (33) becomes, on writing  $k_x = k$ , the ninth degree polynomial

$$\sum_{i=0}^9 A_i n^i = 0 \quad (37)$$

where the coefficients  $A_i$  ( $i = 0$ , to 9) are given in the Appendix.

### Discussion

The dispersion relation given by equation (37) is quite complicated particularly as the coefficients  $A_i$ 's are complex. We have therefore solved the dispersion relation numerically for different values of the parameters characterizing viscosity, streaming motion, surface tension and permeability of the medium. The dispersion relation was of course first non-dimensionalized by measuring  $n$ ,  $v$ ,  $B$ ,  $V$ ,  $Q$  and  $U$  in terms of  $\sqrt{g}$ . For numerical evaluation of the roots of dispersion relation we have taken  $\alpha_1 = 0.25$ ,  $\alpha_2 = 0.75$  (the unstable configuration), Alfvén velocity  $V = 1$  in all the calculations.

These calculations are presented in Figs. 1 to 4 where the growth rate (positive real part of  $n$ ) is plotted against the wave number  $k$  for several values of  $v$ ,  $U$ ,  $B$  and  $Q$ . In Fig. 1, the growth rate is given against the wave number for  $v$  (viscosity) = 0.1, 0.2, 0.3 taking fixed values of  $B$  (surface tension) = 0.1,  $U$  (streaming velocity) = 1,  $Q$  (permeability) = 0.05. From the Fig. 1 we find that the growth rate decreases on increasing the viscosity for same values of the wave number. We thus find that viscosity has stabilizing influence on the Kelvin-Helmholtz instability of the superposed fluids. In Fig. 2 we have given the variation of the growth rate against the wave number for the values of streaming velocity  $U = 2.1, 2.2, 2.3, 2.4$ . In these curves also the values of the other parameters have been kept fixed. From Fig. 2 we

find that the streaming velocity has a destabilizing influence as the growth rate increases with increasing streaming velocity for same values of the wave number. Fig. 3 depicts the variation of the growth rate with surface tension. The curves in the Fig. 3 clearly show that the growth rate decreases with increasing values of  $B$ , the parameter characterizing effect of the surface tension. As the growth rate decreases on increasing the values of  $B$  for same wave number  $k$ . The effect of surface tension is thus stabilizing on the growth rate of the unstable configuration. Fig. 4 gives the plot of growth rate against the wave number for the values of permeability parameter  $Q = 0.2, 0.1, 0.05$ . From Fig. 4, we find that the growth rate decreases on decreasing parameter  $Q$ . The effect of permeability is consequently stabilizing and/or the effect of porosity is destabilizing. These observations are in agreement with the earlier observations of several researchers on the different stability problems.

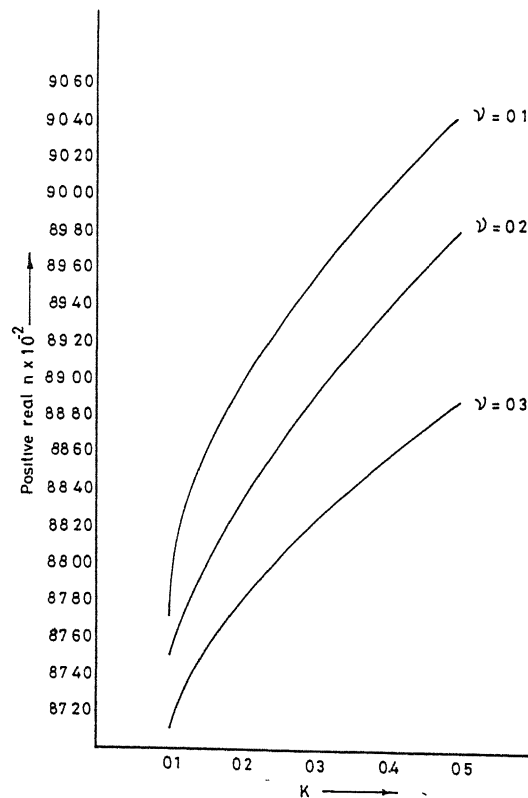


Fig. 1—Variation of growth rate  $n$  against wave number  $K$  for  $v = 0.1, 0.2, 0.3$  taking  $B = 0.1, U = 1.0, Q = 0.2$

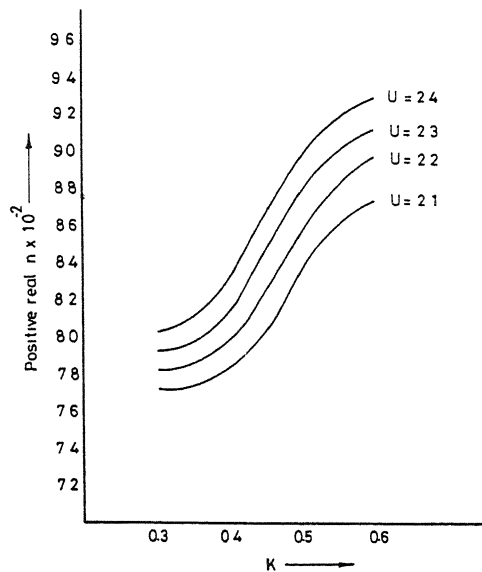


Fig. 2—Variation of growth rate  $n$  against wave number  $K$  for  $U = 2.1, 2.2, 2.3, 2.4$  taking  $\nu=0.1, B=1.0, Q=0.05$

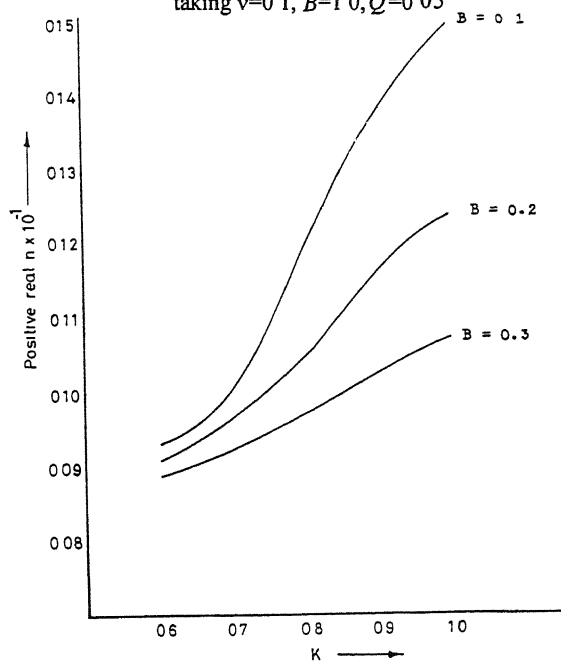


Fig. 3—Variation of growth rate  $n$  against wave number  $K$  for  $B = 0.1, 0.2, 0.3$  taking  $\nu=0.1, U=1.0, Q=0.2$

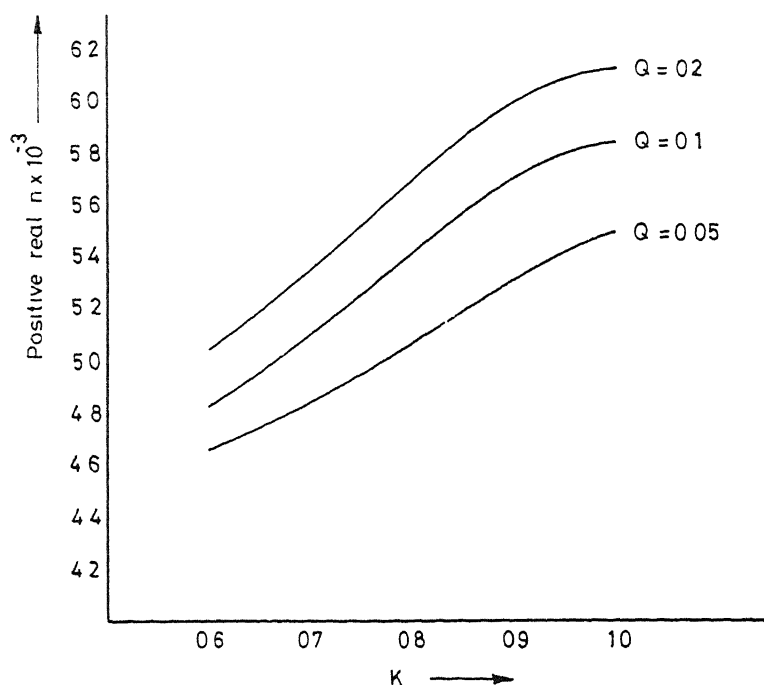


Fig 4-Variation of growth rate  $n$  against wave number  $K$  for  $Q = 0.2, 0.1, 0.05$  taking  $U=1.0, B=0.1$

### References

1. Chandrasekhar, S. (1961) *Hydrodynamic and Hydromagnetic Stability*, Clarendon Press, Oxford.
2. D'Angelo, N. (1965) *Phys Fluids* **8** : 1748.
3. D'Angelo, N. & Von Goeler, S. (1966) *Phys Fluids* **2** : 309.
4. Gerwin, R.A. (1968) *Rev Mod Phys.* **40** : 652.
5. Kalra, G.L., Kathuria, S.N., Hosking, R.J. & Lister, G.C. (1970) *J Plasma Phys* **4** : 451.
6. Bhatia, P.K. & Steiner, J.M. (1974) *Aust J Phys* **27** : 53.
7. Shivamoggi, B.K. (1981) *Physica Scripta* **24** : 49.
8. Sengar, R.S. (1984) *Proc. Nat Acad Sci.* **54(A)** : 438.
9. Mehta, V. & Bhatia, P.K. (1988) *Cont Plasma Phys* **29** : 617.
10. Singh, R.P. & Khare, H.C. (1991) *Proc. Nat Acad Sci.* **43** : 55.
11. Eldabe, N.T. & Hassan, A.A.A. (1991) *Bull. Gal. Math. Soc* **83** : 407.
12. Bhatia, P.K. & Hazarika, A. B. (1995) *Phrsica Scripta.* **38** : 45.

- 13 Benjamin, T B & Bridges, T J (1917) *J Fluid Mech* **333** 301.
- 14 Benjamin, T B & Bridges, T J. (1997) *J Fluid Mech* **333** 326
- 15 Sharma, R C & Kumar, P (1998) *Proc Nat. Acad Sci* **68(A)** : 151
- 16 Allah, M H O. (1998) *Proc Nat Acad Sci* **68(A)** : 163
- 17 McDonnel, J A M (1978) *Cosmic Dust*, John Wiley and Sons, Toronto, p 330
18. Rudraiah, N & Srimani, P K. (1976) *Vignana Bharti* **2( 2 )** 11
- 19 Sharma, B M. (1984) *Jnanabha* **14** 27
- 20 Samra, N K., Reddy, M U.S & Prasad, R (1990) *Astrophys Space Sci* **172** 231
- 21 Sharma, R C & Kumar, P (1995) *Jour Math Phys Sci* **29(2)** 81
- 22 Sunil & Chand, T (1997) *Indian J Phys* **71(B)** 95

# APPENDIX

$$A_9 = 2\alpha_1^2 \alpha_2^2 \gamma^2$$

$$A_8 = \alpha_1 \alpha_2 \gamma \left\{ -21\alpha_1 \alpha_2 \gamma U k (\alpha_2 - \alpha_1) + 4\alpha_1 \alpha_2 \gamma^2 (Q + 2\alpha_1 k^2) \right. \\ \left. + 2\alpha_1 \alpha_2 k^3 B \gamma + 2V^2 (1 - 2\alpha_1 \alpha_2) \right\}$$

$$A_7 = 21Uk \gamma \alpha_1 \alpha_2 (\alpha_2 - \alpha_1) [2\alpha_1 \alpha_2 \gamma^2 Q + V^2 (2 - \alpha_1 \alpha_2)] \\ + 4\alpha_1^2 \alpha_2^2 \gamma^2 k^2 U^2 + \alpha_1 \alpha_2 \left\{ \alpha_1 \alpha_2 \gamma^4 Q (Q + 2k^2 (3\alpha_1 - \alpha_2)) \right. \\ \left. + 4\alpha_1 \alpha_2 \gamma^3 k^3 B Q + \gamma^2 V^2 [4Q(1 - \alpha_1 \alpha_2) - k^2 (4\alpha_1 \alpha_2 (8 - 12\alpha_1 \alpha_2 \right. \\ \left. + \alpha_2 - \alpha_1) - 6)] + 2\gamma k^3 B V^2 (1 - \alpha_1 \alpha_2) \right\}$$

$$A_6 = 1Uk \alpha_1 \alpha_2 \left\{ -4\gamma^2 k^2 U^2 \alpha_1 \alpha_2 (\alpha_2 - \alpha_1) + 2\alpha_1 \alpha_2 \gamma^4 Q [2k^2 (2\alpha_1 - \alpha_2) \right. \\ \left. - Q(\alpha_2 - \alpha_1)] - 4\alpha_1^2 \alpha_2 \gamma^3 k^3 B Q - 2\alpha_1 \alpha_2 \gamma^2 k + \gamma^2 V^2 \{ 3(\alpha_2 - \alpha_1) \right. \\ \left. \cdot (2k^2 - Q(2 - \alpha_1 \alpha_2)) + 2k^2 [(\alpha_2 - \alpha_1)(3\alpha_1 \alpha_2 - 2) + 2 - 9\alpha_1 \alpha_2] \right. \\ \left. + 2Q(\alpha_1^2 \alpha_2 - 1) \right\} - 2k^3 B \gamma V^2 - V^4 (\alpha_2 - \alpha_1) \} \\ + 2\alpha_1 \alpha_2 \gamma k^2 U^2 \left\{ 2\alpha_1 \alpha_2 \gamma^2 (3Q + 8\alpha_1 k^2) + 4\alpha_1 \alpha_2 k^3 B \gamma + V^2 (\alpha_1 \alpha_2 + 2) \right\} \\ - k^2 \gamma V^4 (2 - 7\alpha_1 \alpha_2 + 2\alpha_1^2 \alpha_2^2) - 2\alpha_1^2 \alpha_2^2 \gamma^3 k Q (\alpha_2 - \alpha_1) \\ + \alpha_1 \alpha_2 \gamma V^2 \left\{ k \alpha_1 \alpha_2 (\alpha_2 - \alpha_1) + V^2 (Q - 3k^2) + 2\gamma k^3 B (Q(1 - \alpha_1 \alpha_2) - k^2) \right. \\ \left. + \gamma^2 [Q^2 (2 - 5\alpha_1 \alpha_2) + 2Qk^2 [2(\alpha_2 - \alpha_1) (\alpha_1 \alpha_2 - 1) - 6\alpha_1 \alpha_2 + 1] - 8k^4 \alpha_1] \right\} +$$

$$\begin{aligned}
& + \alpha_1 \alpha_2 \left\{ k^3 B V^4 + \gamma^3 Q [V^2 (3\alpha_1 \alpha_2 Q - 4k^2 (\alpha_2 - \alpha_1) (1 - 2\alpha_1 \alpha_2)) \right. \\
& - 2\alpha_1 \alpha_2 k (\alpha_2 - \alpha_1) + 2\alpha_1 \alpha_2 \gamma Q k^2 (k B - 2\gamma)] + \gamma V^2 [k (\alpha_2 - \alpha_1) \\
& \cdot (\alpha_1 \alpha_2 - 2) + V^2 (2k^2 \alpha_1 (2 - 3\alpha_1) + Q) + 2\gamma k^3 B Q (1 - \alpha_1 \alpha_2)] \left. \right\}
\end{aligned}$$

$$\begin{aligned}
A_5 = & 1kU \left\{ - 6\alpha_1 \alpha_2 k^2 U^2 \gamma (\alpha_2 - \alpha_1) [2\alpha_1 \alpha_2 \gamma^2 Q + V^2 (2 - \alpha_1 \alpha_2)] \right. \\
& + 4k^2 \gamma V^4 (\alpha_2 - \alpha_1) (2 - 3\alpha_1 \alpha_2) + 2\alpha_1 \alpha_2 \gamma \left\{ V^4 (\alpha_2 - \alpha_1) (3k^2 - Q) \right. \\
& - 2\alpha_1 \alpha_2 \gamma^2 k Q + V^2 \left\{ \gamma^2 [Q^2 (\alpha_2 - \alpha_1) (\alpha_1 \alpha_2 - 2) + 2k^2 Q (\alpha_2 - \alpha_1) \right. \\
& \cdot (1 - 2\alpha_1 \alpha_2) - 4\alpha_1 \alpha_2] - 16\alpha_1^2 \alpha_2 k^4] - 5\alpha_1 \alpha_2 k - 2\gamma k^3 B \\
& \cdot (\alpha_2 - \alpha_1) (Q - k^2) \left. \right\} \left. \right\} + 6\alpha_1^2 \alpha_2^2 \gamma^2 U^4 k^4 + \alpha_1 \alpha_2 k^2 U^2 \\
& \cdot \left\{ - \gamma^2 V^2 [Q (2 - 5\alpha_1 \alpha_2) - 2k^2 (1 - 2\alpha_1 \alpha_2)] + 3 \left\{ V^4 + \gamma^2 V^2 \right. \right. \\
& \cdot [Q (\alpha_1 \alpha_2 + 2) + 4k^2 (\alpha_1 \alpha_2 (\alpha_2 - \alpha_1 - 12\alpha_1 \alpha_2 + 7) - 1)] \\
& + 2\gamma k^3 B (2\alpha_1 \alpha_2 \gamma^2 Q + V^2 (1 - \alpha_1 \alpha_2)) + \gamma^4 Q (\alpha_1 \alpha_2 Q \\
& + 2\alpha_1 \alpha_2 k^2 (3\alpha_1 - \alpha_2)) \left. \right\} \left. \right\} + \alpha_1 \alpha_2 \left\{ V^4 [\gamma k^3 B (2Q - 3k^2) - 2V^2 k^2 \right. \\
& - k (\alpha_2 - \alpha_1)] + \gamma^4 k Q \left\{ 4V^2 k [k^2 (\alpha_2 - \alpha_1 - 2\alpha_1 \alpha_2) + Q (\alpha_2 - \alpha_1) \right. \\
& \cdot (\alpha_1 \alpha_2 - 1) - \alpha_1 \alpha_2] - 2\alpha_1 \alpha_2 Q (\alpha_2 - \alpha_1) \left. \right\} + \gamma^2 V^2 \left\{ k (\alpha_2 - \alpha_1) \right. \\
& \cdot (3Q \alpha_1 \alpha_2 + 2(k^2 - 2Q)) + 2\gamma k^3 B Q (Q - k^2 (1 + 2\alpha_1 \alpha_2)) \\
& + V^2 [Q^2 + 4k^4 \alpha_1 (1 - 2\alpha_2) - k^2 Q (2(\alpha_1 \alpha_2 + \alpha_2 - \alpha_1) + 5)] \left. \right\} \left. \right\} \\
& + V^2 \left\{ k^2 V^4 (2\alpha_1 \alpha_2 - 1) - \gamma V^2 k^5 B (2 - 5\alpha_1 \alpha_2) + \right.
\end{aligned}$$

$$\begin{aligned}
& + \gamma^2 \left\{ \alpha_1^2 \alpha_2^2 k Q (\alpha_2 - \alpha_1) + v^2 k^2 [Q (5 \alpha_1 \alpha_2 - 2 \alpha_1^2 \alpha_2^2 - 2) \right. \\
& \left. + 2 k^2 [(\alpha_2 - \alpha_1) (1 - 5 \alpha_1 \alpha_2) + \alpha_1 \alpha_2 (2 \alpha_1 \alpha_2 - 7) + 1] \right\} \Big\} \\
A_4 = & i k U \left\{ - 6 \alpha_1^2 \alpha_2^2 \gamma^2 U^4 k^4 (\alpha_2 - \alpha_1) + \alpha_1 \alpha_2 k^2 U^2 \left\{ 5 \gamma^2 v^2 (\alpha_2 - \alpha_1) \right. \right. \\
& \cdot [2 k^2 - Q (2 - \alpha_1 \alpha_2)] + 2 \gamma^2 v^2 \left\{ k^2 [(\alpha_2 - \alpha_1) (3 \alpha_1 \alpha_2 - 2) \right. \\
& + (2 - 9 \alpha_1 \alpha_2)] + Q (\alpha_1^2 \alpha_2 - 1) \Big\} + 2 \alpha_1 \alpha_2 \gamma^4 Q [2 k^2 (2 \alpha_1 - \alpha_2) \\
& - Q (\alpha_2 - \alpha_1)] - 2 \alpha_1 \alpha_2 \gamma^2 k - (\alpha_2 - \alpha_1) v^4 - 2 k^3 B \gamma [2 \alpha_1^2 \alpha_2 \gamma^2 Q \\
& + v^2] \Big\} \Big\} + \alpha_1 \alpha_2 \left\{ 2 k^2 v^6 (\alpha_2 - \alpha_1) + v^4 \left\{ \gamma^2 [(\alpha_2 - \alpha_1) (3 k^2 (Q - k^2) \right. \right. \\
& - Q^2) + 2 k^2 (4 \alpha_1 \alpha_2 - 1) (2 (Q + k^2 (k^2 - 1)) + k^2 Q)] - k - \gamma k^5 B (\alpha_2 - \alpha_1) \Big\} \\
& + \gamma^2 v^2 k [2 k (2 \alpha_1 \alpha_2 - 1) - 3 \alpha_1 \alpha_2 Q - \gamma k^3 B Q (Q - k^2) (\alpha_2 - \alpha_1)] \Big\} \Big\} \\
& + 3 v^2 \left\{ - \alpha_1^2 \alpha_2^2 \gamma^2 k (3 Q - 4 k^2) + v^2 (\alpha_2 - \alpha_1) [v^2 k^2 (2 \alpha_1 \alpha_2 - 1) \right. \\
& + \gamma k^5 B (2 - \alpha_1 \alpha_2) + \gamma^2 k^2 [Q (5 \alpha_1 \alpha_2 - 2) + 4 k^2 (1 + 2 \alpha_1 \alpha_2 (1 - 2 \alpha_1 \alpha_2)) \\
& + 2 (Q + 2 \alpha_1^2 \alpha_2)] \Big\} \Big\} + 2 \alpha_1 \alpha_2 k^4 U^4 \gamma \left\{ 5 [2 \alpha_1 \alpha_2 \gamma^2 Q \right. \\
& + v^2 (2 - 5 \alpha_1 \alpha_2)] + 3 \alpha_1 \alpha_2 [2 \gamma^2 (Q + 4 \alpha_1 k^2) + 2 k^3 B \gamma + 3 v^2] \Big\} \\
& + k^2 U^2 \left\{ 5 \gamma v^4 k^2 (2 - 7 \alpha_1 \alpha_2 + 2 \alpha_1^2 \alpha_2^2) - 2 \alpha_1^2 \alpha_2^2 \gamma^3 k Q (\alpha_2 - \alpha_1) \right. \\
& + \alpha_1 \alpha_2 \gamma v^2 \left\{ k \alpha_1 \alpha_2 (\alpha_2 - \alpha_1) + v^2 (Q - 3 k^2) + 2 \gamma k^3 B (Q (1 - \alpha_1 \alpha_2) - k^2) \right. \\
& + \gamma^2 [Q^2 (2 - 5 \alpha_1 \alpha_2) + 2 Q k^2 (2 (\alpha_2 - \alpha_1) (\alpha_1 \alpha_2 - 1) - 6 \alpha_1 \alpha_2 + 1) - 8 k^4 \alpha_1] \Big\} \\
& + 3 \alpha_1 \alpha_2 \left\{ k^3 B v^4 + \gamma^3 Q [v^2 (3 \alpha_1 \alpha_2 Q - 4 k^2 (\alpha_2 - \alpha_1) (1 - 2 \alpha_1 \alpha_2)) - \right.
\end{aligned}$$

$$\begin{aligned}
& - 2\alpha_1\alpha_2k(\alpha_2-\alpha_1)+2\alpha_1\alpha_2k^2Q\gamma(kB-2\gamma)+\gamma v^2[k(\alpha_2-\alpha_1)(\alpha_1\alpha_2-2) \\
& + v^2(2k^2\alpha_1(2-3\alpha_1)+Q)+2\gamma k^3BQ(1-\alpha_1\alpha_2)]\}\} + \gamma v^2\{k^3B\gamma v^2 \\
& \cdot [2k^2Q((\alpha_2-\alpha_1)(1-\alpha_1\alpha_2)-2\alpha_1\alpha_2)+\alpha_1\alpha_2(Q^2+2k^4)] \\
& + k v^2(\alpha_2-\alpha_1)[2k^2(1-2\alpha_1\alpha_2)+\alpha_1\alpha_2(\alpha_2-\alpha_1)(Q-1)] \\
& + \alpha_1\alpha_2kQ\gamma^2(\alpha_2-\alpha_1)[2Q(1-\alpha_1\alpha_2)+k^2(3\alpha_1\alpha_2-2)]+v^4\{k^2Q \\
& \cdot [(\alpha_2-\alpha_1)(\alpha_1\alpha_2-1)-5\alpha_1\alpha_2]+2k^4[(\alpha_2-\alpha_1)(1-5\alpha_1\alpha_2)-3] \\
& + \alpha_1\alpha_2(2k^2+Q)]\} + 2k^2\gamma^2v^2\{\alpha_1\alpha_2Q[(4\alpha_1\alpha_2-1)+Q(1-3(\alpha_2-\alpha_1) \\
& - 6\alpha_1\alpha_2)]+k^2[2\alpha_1\alpha_2(k^2(4\alpha_1\alpha_2-\alpha_2+\alpha_1)-2\alpha_1\alpha_2) \\
& + Q(1-2\alpha_1\alpha_2(3-4\alpha_1\alpha_2)+(\alpha_2-\alpha_1)(4\alpha_1\alpha_2-1))]\}\}
\end{aligned}$$

$$\begin{aligned}
A_3 = & iUk\left\{-26\alpha_1\alpha_2k^4U^4\gamma(\alpha_2-\alpha_1)[2\alpha_1\alpha_2\gamma^2Q+v^2(2-\alpha_1\alpha_2)]\right. \\
& + k^2U^2\left\{4\alpha_1\alpha_2\gamma\left\{v^4(\alpha_2-\alpha_1)(3k^2-Q)-2\alpha_1\alpha_2\gamma^2kQ\right.\right. \\
& + v^2\left\{\gamma^2[Q^2(\alpha_2-\alpha_1)(\alpha_1\alpha_2-2)+2k^2Q((\alpha_2-\alpha_1)(1-2\alpha_1\alpha_2) \right. \\
& - 4\alpha_1\alpha_2)-16\alpha_1^2\alpha_2k^4]-5\alpha_1\alpha_2k-2\gamma k^3B(\alpha_2-\alpha_1)(Q-k^2)]\}\} \\
& - 9\alpha_1\alpha_2\left\{v^4k^3B-2\alpha_1\alpha_2\gamma^3Qk[(\alpha_2-\alpha_1)+2\gamma^2Qk-\gamma k^3BQ] \right. \\
& + \gamma v^2\left\{v^2(2\alpha_1\alpha_2(Q+3k^2)-2k^2(\alpha_2-\alpha_1))+\gamma^2Q[2\alpha_1\alpha_2(Q+k^2) \right. \\
& + 4k^2(\alpha_2-\alpha_1)(2\alpha_1\alpha_2-1)]+2\gamma k^3BQ(1-\alpha_1\alpha_2)-k(\alpha_2-\alpha_1) \\
& \cdot (2-\alpha_1\alpha_2)]\}\}\} + 2\left\{4\alpha_1\alpha_2\gamma v^4k^3(1-\alpha_1\alpha_2) - \right.
\end{aligned}$$

$$\begin{aligned}
& - v^2 \{ k^5 B v^4 (1-2\alpha_1 \alpha_2) + \gamma^3 \alpha_1^2 \alpha_2^2 k Q (3Q-4k^2) + \gamma v^2 k [k^2 \\
& \cdot (2-9\alpha_1 \alpha_2 + 4\alpha_1^2 \alpha_2^2) + \alpha_1 \alpha_2 Q] + \gamma^2 v^2 k^5 B [2Q(1-3\alpha_1 \alpha_2) \\
& - \alpha_1 \alpha_2 (\alpha_2 - \alpha_1)] + \gamma k^2 v^4 \{ k^2 [(\alpha_2 - \alpha_1)(7\alpha_1 \alpha_2 - 2) \\
& + 4\alpha_1 \alpha_2 (1-4\alpha_1 \alpha_2) - 2] + (\alpha_2 - \alpha_1) [4k^4 (3\alpha_1 \alpha_2 - 1) - 4\alpha_1 \alpha_2 Q] \} \\
& - 2\alpha_1 \alpha_2 \gamma^3 v^2 k^2 Q [k^2 (2(\alpha_2 - \alpha_1) - 12\alpha_1 \alpha_2 + 11) + Q(\alpha_2 - \alpha_1)] \} \} \\
& + 4\alpha_1^2 \alpha_2^2 \gamma^2 k^6 U^6 + \alpha_1 \alpha_2 k^4 U^4 \{ -25 \gamma^2 v^2 [Q(2-5\alpha_1 \alpha_2) \\
& - 2k^2 (1-2\alpha_1 \alpha_2)] + 11 [v^4 + \gamma^2 v^2 [Q(\alpha_1 \alpha_2 + 2) + 4k^2 (\alpha_1 \alpha_2 \\
& \cdot (\alpha_2 - \alpha_1 - 12\alpha_1 \alpha_2 + 7) - 1)] + 2 \gamma k^3 B (2\alpha_1 \alpha_2 \gamma^2 Q + v^2 (1 - \alpha_1 \alpha_2)) \\
& + \gamma^4 Q (\alpha_1 \alpha_2 Q + 2\alpha_1 \alpha_2 k^2 (3\alpha_1 - \alpha_2))] \} + 2k^2 U^2 \{ \alpha_1 \alpha_2 \{ v^4 [\gamma B k^3 \\
& \cdot (2Q-3k^2) - 2v^2 k^2 - k(\alpha_2 - \alpha_1)] + \gamma^4 k Q \{ 4v^2 k [k^2 (\alpha_2 - \alpha_1 - 2\alpha_1 \alpha_2) \cdot \\
& + Q((\alpha_2 - \alpha_1)(\alpha_1 \alpha_2 - 1) - \alpha_1 \alpha_2)] - 2\alpha_1 \alpha_2 Q(\alpha_2 - \alpha_1) \} \\
& + \gamma^2 v^2 \{ k(\alpha_2 - \alpha_1)(3Q\alpha_1 \alpha_2 + 2(k^2 - 2Q)) + 2 \gamma k^3 B Q(Q \\
& - k^2 (2\alpha_1 \alpha_2 + 1)) + v^2 [Q^2 + 4k^4 \alpha_1 (1-2\alpha_2) - k^2 Q(2(\alpha_1 \alpha_2 + \alpha_2 - \alpha_1) \\
& + 5)] \} \} - v^2 \{ k^2 v^4 (2\alpha_1 \alpha_2 - 1) - \gamma v^2 k^5 B (2-5\alpha_1 \alpha_2) \\
& + \gamma^2 \{ \alpha_1^2 \alpha_2^2 k Q (\alpha_2 - \alpha_1) + v^2 k^2 [Q(5\alpha_1 \alpha_2 - 2\alpha_1^2 \alpha_2^2 - 2) \\
& + 2k^2 [(\alpha_2 - \alpha_1)(1-5\alpha_1 \alpha_2) + \alpha_1 \alpha_2 (2\alpha_1 \alpha_2 - 7) + 1]] \} \} \\
& + 2\alpha_1 \alpha_2 k^3 v^4 (\gamma^2 Q(1-2\alpha_1 \alpha_2) + \alpha_2 v^2) + v^4 \{ \gamma^2 k [k^2 Q(4\alpha_1 \alpha_2 \\
& \cdot (3\alpha_2 + \alpha_1 - \alpha_1 \alpha_2) - 2) - \alpha_1 \alpha_2 (\alpha_2 - \alpha_1)(Q^2 + 2k^4)] +
\end{aligned}$$

$$\begin{aligned}
& + v^2 \{ v^2 k^4 + k^2 (2\alpha_1 \alpha_2 (2\alpha_2 + \alpha_1) - 1) - \gamma k^5 B [Q - 2k^2 + 2\alpha_1 \alpha_2 \\
& \cdot (3k^2 - 2Q)] + 2 \gamma^2 k^2 \alpha_1 [2k^2 Q (2\alpha_1 (2\alpha_2 - \alpha_1) - 1) \\
& + 4\alpha_1 \alpha_2 k^2 + \alpha_2 Q (1 - Q) - 4k^4 (1 + 4\alpha_2^2)] \} \}
\end{aligned}$$

$$\begin{aligned}
A_2 = & 1Uk \{ 4\alpha_1^2 \alpha_2^2 \gamma^2 k^6 U^6 (\alpha_2 - \alpha_1) + \alpha_1 \alpha_2 k^4 U^4 \{ \gamma^2 v^2 (\alpha_2 - \alpha_1) \\
& \cdot [2k^2 - Q (2 - \alpha_1 \alpha_2)] + 15 [ \gamma^2 v^2 k^2 [2(\alpha_2 - \alpha_1) (3\alpha_1 \alpha_2 - 2) \\
& + 2(2 - 9\alpha_1 \alpha_2)] + 2 \gamma^2 v^2 Q [\alpha_1^2 \alpha_2 - 1] + 2\alpha_1 \alpha_2 \gamma^4 Q [2k^2 (2\alpha_1 - \alpha_2) \\
& - Q(\alpha_2 - \alpha_1)] - 2\alpha_1 \alpha_2 \gamma^2 k - v^4 (\alpha_2 - \alpha_1) - 2k^3 B \gamma (2\alpha_1^2 \alpha_2 \gamma^2 Q + v^2) \} \\
& + 2k^2 U^2 \{ 2\alpha_1 \alpha_2 \{ 2k^2 v^6 (\alpha_2 - \alpha_1) + v^4 \{ \gamma^2 [(\alpha_2 - \alpha_1) (3k^2 (Q - k^2) \\
& - Q^2) + 2k^2 (4\alpha_1 \alpha_2 - 1) (2(Q + k^2 (k^2 - 1)) + k^2 Q)] - k \\
& - \gamma k^5 B (\alpha_2 - \alpha_1) \} + \gamma^2 v^2 k [2k (2\alpha_1 \alpha_2 - 1) - 3\alpha_1 \alpha_2 Q \\
& - \gamma k^2 Q B (Q - k^2) (\alpha_2 - \alpha_1)] \} + v^2 \{ -\alpha_1^2 \alpha_2^2 \gamma^2 k (3Q - 4k^2) \\
& + v^2 (\alpha_2 - \alpha_1) [v^2 k^2 (2\alpha_1 \alpha_2 - 1) + \gamma k^5 B (2 - \alpha_1 \alpha_2) + \gamma^2 k^2 \\
& \cdot [Q (5\alpha_1 \alpha_2 - 2) + 4k^2 (1 + 2\alpha_1 \alpha_2 (1 - 2\alpha_1 \alpha_2)) + 2(Q + 2\alpha_1^2 \alpha_2)] \} \} \\
& + 3 [2\alpha_1 \alpha_2 v^4 k^3 (\gamma^2 (\alpha_1 \alpha_2 - \alpha_2 + \alpha_1) + \alpha_1 v^2)] - v^4 \{ v^4 k^4 (\alpha_2 - \alpha_1) \\
& - k^3 v^2 [(\alpha_2 - \alpha_1) (1 - \alpha_1 \alpha_2) - \alpha_1 \alpha_2 + \gamma k^2 B (\alpha_2 - \alpha_1) (Q - 2k^2)] \\
& + \gamma^2 \{ k [\alpha_1 \alpha_2 (Q - k^2) (Q - 2k^2) - k^2 Q (1 - 2\alpha_1 \alpha_2) (2(\alpha_2 - \alpha_1) + \alpha_1 \alpha_2)] \\
& + 2v^2 k^2 [(\alpha_2 - \alpha_1) [(2k^2 + Q) (k^2 - \alpha_1 \alpha_2 (2k^2 + Q)) - 2\alpha_1 \alpha_2 k^4] +
\end{aligned}$$

$$\begin{aligned}
& + k^2 [2(1-4\alpha_1\alpha_2 + \alpha_1\alpha_2(5k^2-4)) + Q(1-3\alpha_1\alpha_2)] \} \} \} \\
& - 2k^6 U^6 \alpha_1\alpha_2 \gamma \{ 11[2\alpha_1\alpha_2 \gamma^2 Q + v^2(2-5\alpha_1\alpha_2)] - 2\alpha_1\alpha_2 [2 \gamma^2 \\
& \cdot (Q+4\alpha_1 k^2) + 2k^3 B \gamma + 3v^2] \} + k^4 U^4 \{ 5k^2 \gamma v^4(2-7\alpha_1\alpha_2 + 2\alpha_1^2\alpha_2^2) \\
& - \alpha_1\alpha_2 \gamma \{ v^2 \{ \alpha_1\alpha_2 k(\alpha_2-\alpha_1) + v^2(4-3k^2) + 2\gamma k^3 B(Q(1-\alpha_1\alpha_2) \\
& - k^2) + \gamma^2 \{ Q^2(2-5\alpha_1\alpha_2) + 2Qk^2[2(\alpha_2-\alpha_1)(\alpha_1\alpha_2-1) - 6\alpha_1\alpha_2+1] \\
& - 8k^4\alpha_1 \} \} - 2\alpha_1\alpha_2 \gamma^2 kQ(\alpha_2-\alpha_1) \} + 15\alpha_1\alpha_2 \{ k^3 B v^4 \\
& + \gamma^3 Q[v^2(3\alpha_1\alpha_2 Q - 4k^2(\alpha_2-\alpha_1)(1-2\alpha_1\alpha_2) - 2\alpha_1\alpha_2 k(\alpha_2-\alpha_1) \\
& + 2\alpha_1\alpha_2 \gamma Qk^2(kB-2\gamma) + \gamma v^2[k(\alpha_2-\alpha_1)(\alpha_1\alpha_2-2) + v^2 \\
& + (2k^2\alpha_1(2-3\alpha_1) + Q) + 2\gamma k^3 BQ(1-\alpha_1\alpha_2)] \} \} + k^2 U^2 \\
& \cdot 12\alpha_1\alpha_2 \gamma v^4 k^3(\alpha_2-\alpha_1) + 2\alpha_1\alpha_2 \gamma v^2 \{ v^2 k[(Q-k^2)((\alpha_2-\alpha_1) \\
& + \gamma k^3 B(Q-2k^2)) - v^2 k(2Q-3k^2)] + \gamma^2 \{ kQ(Q-k^2)(\alpha_2-\alpha_1)(2-3\alpha_1\alpha_2) \\
& + 2v^2 k^2 [Q^2(2\alpha_1\alpha_2 - \alpha_2 + \alpha_1) + 2k^4(4\alpha_1\alpha_2 - \alpha_2 + \alpha_1) + 3k^2 Q(\alpha_2 - \alpha_1) \\
& + 2(4\alpha_1\alpha_2 - 1)(Q - k^2)] \} \} \} + k^3 v^6 \{ \gamma(\alpha_2 - \alpha_1)[(Q - 2k^2) \\
& \cdot (1 - \alpha_1\alpha_2) + \alpha_1\alpha_2(Q - k^2)] + k^4 B v^2 + 2\gamma v^2 k[2\alpha_1\alpha_2(2k^2 + Q) \\
& + (\alpha_2 - \alpha_1)(k^2 + Q)] + \alpha_1\alpha_2 \gamma [(Q - k^2)(\alpha_2 - \alpha_1) - (Q - 2k^2)] \} \\
A_1 = & 1kU \{ 8\alpha_1\alpha_2 \gamma k^6 U^6 (\alpha_2 - \alpha_1) [2\alpha_1\alpha_2 \gamma^2 Q + v^2(2 - \alpha_1\alpha_2)] + k^4 U^4 \\
& \cdot \{ -4k^2 \gamma v^4(2 - 3\alpha_1\alpha_2) + 2\alpha_1\alpha_2 \gamma \{ v^4(\alpha_2 - \alpha_1)(3k^2 - Q) -
\end{aligned}$$

$$\begin{aligned}
& - 2\alpha_1\alpha_2 \gamma^2 k Q + v^2 \left\{ \gamma^2 [Q^2(\alpha_2 - \alpha_1)(\alpha_1\alpha_2 - 2) + 2k^2 Q(\alpha_2 - \alpha_1)] \right. \\
& \cdot (1 - 2\alpha_1\alpha_2) - 4\alpha_1\alpha_2 - 16\alpha_1^2\alpha_2 k^4 - 5\alpha_1\alpha_2 k - 2 \gamma k^3 B(\alpha_2 - \alpha_1) \\
& \cdot (Q - k^2) \left. \right\} - 4k^2 U^2 \left\{ 2\alpha_1\alpha_2 \gamma v^4 k^3 (1 - \alpha_1\alpha_2) + v^2 \left\{ k^5 B v^4 \right. \right. \\
& \cdot (1 - 2\alpha_1\alpha_2) + \gamma^3 \alpha_1^2 \alpha_2^2 k Q (3Q - 4k^2) + \gamma v^2 k [k^2 (2 - 9\alpha_1\alpha_2 + 4\alpha_1^2 \alpha_2^2) \\
& + \alpha_1\alpha_2 Q] + \gamma^2 v^2 k^5 B [2Q(1 - 3\alpha_1\alpha_2) - \alpha_1\alpha_2(\alpha_2 - \alpha_1)] \\
& + \gamma k^2 v^4 \left\{ k^2 [(\alpha_2 - \alpha_1)(7\alpha_1\alpha_2 - 2) + 4\alpha_1\alpha_2(1 - 4\alpha_1\alpha_2) - 2] \right. \\
& + (\alpha_2 - \alpha_1) [4k^4(3\alpha_1\alpha_2 - 1) - 4\alpha_1\alpha_2 + Q] \left. \right\} - 2\alpha_1\alpha_2 \gamma^3 v^2 k^2 Q \\
& \cdot [k^2(2(\alpha_2 - \alpha_1) - 12\alpha_1\alpha_2 + 11) + Q(\alpha_2 - \alpha_1)] \left. \right\} + 2[\alpha_1\alpha_2 \gamma v^6 k^3 \\
& \cdot (Q - k^2) + \alpha_1\alpha_2(\alpha_2 - \alpha_1) \gamma v^6 k^3 (Q - 2k^2)] + \alpha_1^2 \alpha_2^2 \gamma^2 k^8 U^8 \\
& + \alpha_1\alpha_2 k^6 U^6 \left\{ 3 \gamma^2 v^2 [Q(2 - 5\alpha_1\alpha_2) - 2k^2(1 - 2\alpha_1\alpha_2)] \right. \\
& - 7 \left\{ v^4 + \gamma^2 v^2 [Q(\alpha_1\alpha_2 + 2) + 4k^2(\alpha_1\alpha_2(\alpha_2 - \alpha_1 + 7 - 12\alpha_1\alpha_2) - 1)] \right. \\
& + 2 \gamma k^3 B(2\alpha_1\alpha_2 \gamma^2 Q + v^2(1 - \alpha_1\alpha_2)) + \gamma^4 Q(\alpha_1\alpha_2 Q + 2\alpha_1\alpha_2 k^2 \\
& \cdot (3\alpha_1 - \alpha_2) \left. \right\} + k^4 U^4 \left\{ 5\alpha_1\alpha_2 \left\{ v^4 [\gamma k^3 B(2Q - 3k^2) - 2v^2 k^2 \right. \right. \\
& - k(\alpha_2 - \alpha_1)] + \gamma^4 k Q \left\{ 4v^2 k [k^2(\alpha_2 - \alpha_1 - 2\alpha_1\alpha_2) + Q(\alpha_2 - \alpha_1) \right. \\
& \cdot (\alpha_1\alpha_2 - 1) - \alpha_1\alpha_2] - 2\alpha_1\alpha_2 Q(\alpha_2 - \alpha_1) \left. \right\} + \gamma^2 v^2 \left\{ k(\alpha_2 - \alpha_1) \right. \\
& \cdot (3Q\alpha_1\alpha_2 + 2(k^2 - 2Q)) + 2 \gamma k^3 B Q(Q - k^2(2\alpha_1\alpha_2 + 1)) \\
& + v^2 [Q^2 + 4k^4 \alpha_1(1 - 2\alpha_2) - k^2 Q(2(\alpha_1\alpha_2 + \alpha_2 - \alpha_1) + 5)] \left. \right\} \left. \right\} -
\end{aligned}$$

$$\begin{aligned}
& - 3V^2 \{ k^2 V^4 (2\alpha_1 \alpha_2 - 1) - \gamma V^2 k^5 B (2 - 5\alpha_1 \alpha_2) + \gamma^2 \{ \alpha_1^2 \alpha_2^2 k Q \\
& \cdot (\alpha_2 - \alpha_1) + V^2 k^2 [Q(5\alpha_1 \alpha_2 - 2\alpha_1^2 \alpha_2^2 - 2) + 2k^2 ((\alpha_2 - \alpha_1)(1 - 5\alpha_1 \alpha_2) \\
& + \alpha_1 \alpha_2 (2\alpha_1 \alpha_2 - 7) + 1)] \} \} + k^2 U^2 \{ -6\alpha_1 \alpha_2 k^3 V^4 (\gamma^2 Q (1 - 2\alpha_1 \alpha_2) \\
& + \alpha_2 V^2) + V^4 \{ \gamma^2 k [k^2 Q (4\alpha_1 \alpha_2 (3\alpha_2 + \alpha_1 - \alpha_1 \alpha_2) - 2) \\
& - \alpha_1 \alpha_2 (\alpha_2 - \alpha_1) (Q^2 + 2k^4)] + V^2 \{ k^4 V^4 + k^3 (2\alpha_1 \alpha_2 (2\alpha_2 + \alpha_1) - 1) \\
& - \gamma k^5 B [Q - 2k^2 + 2\alpha_1 \alpha_2 (3k^2 - 2Q)] + 2\gamma^2 k^2 \alpha_1 [2k^2 Q (2\alpha_1 (2\alpha_2 - \alpha_1) \\
& - 1) + 4\alpha_1 \alpha_2 k^2 + \alpha_2 Q (1 - Q) - 4k^4 (1 + 4\alpha_2^2)] \} \} \} - k^5 V^8 (\alpha_2 - \alpha_1 - 2\alpha_1 \alpha_2) \\
& = 1kU \{ -\alpha_1^2 \alpha_2^2 \gamma^2 k^8 U^8 (\alpha_2 - \alpha_1) - \alpha_1 \alpha_2 k^6 U^6 \{ \gamma^2 V^2 (\alpha_2 - \alpha_1) \\
& \cdot [Q(2 - \alpha_1 \alpha_2) - 2k^2] + \gamma^2 V^2 \{ k^2 [2(\alpha_2 - \alpha_1) (3\alpha_1 \alpha_2 - 2) \\
& + 2(2 - 9\alpha_1 \alpha_2)] + 2Q(\alpha_1^2 \alpha_2 - 1) \} + 2\alpha_1 \alpha_2 \gamma^4 Q [2k^2 (2\alpha_1 - \alpha_2) \\
& - Q(\alpha_2 - \alpha_1)] - 2\alpha_1 \alpha_2 \gamma^2 k - V^4 (\alpha_2 - \alpha_1) - 2k^3 B \gamma [2\alpha_1^2 \alpha_2 \gamma^2 Q + V^2] \} \\
& - k^4 U^4 \{ \alpha_1 \alpha_2 \{ 2k^2 V^6 (\alpha_2 - \alpha_1) + V^4 \{ \gamma^2 [(\alpha_2 - \alpha_1) (3k^2 (Q - k^2) - Q^2) \\
& + 2k^2 (4\alpha_1 \alpha_2 - 1) (2(Q + k^2 (k^2 - 1)) + k^2 Q)] - k - \gamma k^5 B (\alpha_2 - \alpha_1) \} \\
& + \gamma^2 V^2 k [2k (2\alpha_1 \alpha_2 - 1) - 3\alpha_1 \alpha_2 Q - \gamma k^3 B Q (Q - k^2) (\alpha_2 - \alpha_1)] \} + V^2 \\
& \cdot \{ -\alpha_1^2 \alpha_2^2 \gamma^2 k (3Q - 4k^2) + V^2 (\alpha_2 - \alpha_1) [V^2 k^2 (2\alpha_1 \alpha_2 - 1) + \gamma k^5 B \\
& \cdot (2 - \alpha_1 \alpha_2) + \gamma^2 k^2 [Q(5\alpha_1 \alpha_2 - 2) + 4k^2 (1 + 2\alpha_1 \alpha_2 (1 - 2\alpha_1 \alpha_2)) \\
& + 2(Q + 2\alpha_1^2 \alpha_2)] \} \} + k^2 U^2 \{ 2\alpha_1 \alpha_2 V^4 k^3 [\gamma^2 (\alpha_1 \alpha_2 - \alpha_2 + \alpha_1) +
\end{aligned}$$

$$\begin{aligned}
& + \alpha_1 v^2) ] - v^4 \{ k^4 v^4 (\alpha_2 - \alpha_1) - k^3 v^2 [(\alpha_2 - \alpha_1)(1 - \alpha_1 \alpha_2) - \alpha_1 \alpha_2 \\
& + \gamma k^2 B(Q - 2k^2)(\alpha_2 - \alpha_1)] + \gamma^2 \{ k [\alpha_1 \alpha_2 (Q - k^2)(Q - 2k^2) \\
& - k^2 Q(1 - 2\alpha_1 \alpha_2)(2(\alpha_2 - \alpha_1) + \alpha_1 \alpha_2)] + 2v^2 k^2 [(\alpha_2 - \alpha_1) \\
& \cdot [(2k^2 + Q)(k^2 - \alpha_1 \alpha_2(2k^2 + Q)) - 2\alpha_1 \alpha_2 k^4] + k^2 [2(1 - 4\alpha_1 \alpha_2 \\
& + \alpha_1 \alpha_2(5k^2 - 1)) + Q(1 - 3\alpha_1 \alpha_2)] \} \} \} - k^5 v^8 (1 - 2\alpha_1 \alpha_2) \} \\
& - \alpha_1 \alpha_2 \gamma k^8 u^8 \{ 2\alpha_1 \alpha_2 \gamma^2 Q + v^2(2 - 5\alpha_1 \alpha_2) + \alpha_1 \alpha_2 [2\gamma^2(Q + 4\alpha_1 k^2) \\
& + 2k^3 B\gamma + 3v^2] \} + k^6 u^6 \{ - \gamma k^2 v^4(2 - 7\alpha_1 \alpha_2 + 2\alpha_1^2 \alpha_2^2) - \alpha_1 \alpha_2 \gamma \\
& \cdot \{ v^2 \{ \alpha_1 \alpha_2 k(\alpha_2 - \alpha_1) + v^2(Q - 3k^2) + 2\gamma k^3 B(Q(1 - \alpha_1 \alpha_2) - k^2) \\
& + \gamma^2 \{ Q^2(2 - 5\alpha_1 \alpha_2) + 2Qk^2 [2(\alpha_2 - \alpha_1)(\alpha_1 \alpha_2 - 1) - 5\alpha_1 \alpha_2 - 1] \\
& - 8k^4 \alpha_1 \} \} \} - 2\alpha_1 \alpha_2 \gamma^2 k Q(\alpha_2 - \alpha_1) \} + \alpha_1 \alpha_2 \{ k^3 B v^4 \\
& + \gamma^3 Q [v^2(3\alpha_1 \alpha_2 Q - 4k^2(\alpha_2 - \alpha_1)(1 - 2\alpha_1 \alpha_2)) - 2\alpha_1 \alpha_2 k(\alpha_2 - \alpha_1) \\
& + 2\alpha_1 \alpha_2 \gamma Q k^2(Bk - 2\gamma)] + \gamma v^2 [k(\alpha_2 - \alpha_1)(\alpha_1 \alpha_2 - 2) + v^2(2k^2 \alpha_1 \\
& \cdot (2 - 3\alpha_1) + Q) + 2\gamma k^3 B Q(1 - \alpha_1 \alpha_2)] \} \} + k^4 u^4 \{ v^6 k^5 B(\alpha_2 - \alpha_1 \\
& - 2\alpha_1 \alpha_2) + \gamma v^2 \{ k^3 B \gamma v^2 [2k^2 Q((\alpha_2 - \alpha_1)(1 - \alpha_1 \alpha_2) - 2\alpha_1 \alpha_2) \\
& + \alpha_1 \alpha_2(Q^2 + 2k^4)] + k v^2(\alpha_2 - \alpha_1) [2k^2(1 - 2\alpha_1 \alpha_2) + \alpha_1 \alpha_2(\alpha_2 - \alpha_1) \\
& \cdot (Q - 1)] + \alpha_1 \alpha_2 k Q \gamma^2(\alpha_2 - \alpha_1) [2Q(1 - \alpha_1 \alpha_2) + k^2(3\alpha_1 \alpha_2 - 2)] \\
& + v^4 \{ k^2 Q [(\alpha_2 - \alpha_1)(\alpha_1 \alpha_2 - 1) - 5\alpha_1 \alpha_2] + 2k^4 [(\alpha_2 - \alpha_1)(1 - 5\alpha_1 \alpha_2) - 3] +
\end{aligned}$$

$$\begin{aligned}
& + \alpha_1 \alpha_2 (2k^2 + 1) \} + 2k^2 \gamma^2 v^2 \{ \alpha_1 \alpha_2 Q [4\alpha_1 \alpha_2 - 1 + Q(1 - 3(\alpha_2 - \alpha_1) \\
& - 6\alpha_1 \alpha_2)] + k^2 [2\alpha_1 \alpha_2 (k^2 (4\alpha_1 \alpha_2 - \alpha_2 + \alpha_1) - 2\alpha_1 \alpha_2] \\
& + Q(1 - 2\alpha_1 \alpha_2 (3 - 4\alpha_1 \alpha_2)) + (\alpha_2 - \alpha_1)(4\alpha_1 \alpha_2 - 1)) \} \} \\
& + k^2 U^2 \{ v^6 k^3 \{ \gamma (\alpha_2 - \alpha_1) [(Q - 2k^2)(1 - \alpha_1 \alpha_2) + \alpha_1 \alpha_2 (Q - k^2)] \\
& + k^4 B V^2 + 2 \gamma k V^2 [2\alpha_1 \alpha_2 (2k^2 + Q) + (\alpha_2 - \alpha_1)(k^2 + Q)] \\
& - \alpha_1 \alpha_2 \gamma [(Q - k^2)(\alpha_2 - \alpha_1) - (Q - 2k^2)] \} \}
\end{aligned}$$

## Area-time tradeoffs for parallel merging

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### Abstract

In this paper, the VLSI complexity for the problem of merging two sorted arrays is studied. Let  $A$  and  $T$  be the chip area and computation time of a VLSI circuit that merges two sorted arrays of length  $N$ , by deriving the information transfer between the two sides of a partition of the chip, it is shown that  $AT^2 = \Omega(N^2 \log^2 N)$ . This result indicates that the inherent computational complexities for sorting and merging are asymptotically identical in the VLSI mode, unlike in the conventional model of sequential computation.

(**Keywords** : VLSI algorithms/parallel merging/area-time tradeoffs/computational complexities)

### Introduction

With the advent of Very Large Scale Integration (VLSI), the chip area and computation time have been reduced dramatically. As a result, new methodologies and techniques are employed to design and manufacture small and expensive chips. Since in VLSI the wires, as opposed to the processing elements, dominate the manufacturing cost and computation time, the chip area rather than the number of logical elements is counted as the main measure of the complexity of the computation. Details on VLSI technology are discussed in Mead and Conway<sup>1</sup>.

One important and interesting area in VLSI research is to obtain lower bounds for the area-time tradeoffs for certain problems. During the past few years, various models for VLSI computation were developed<sup>1-5</sup>. Based on these models lower bounds for area - time tradeoffs are obtained for problems such as discrete Fourier transform<sup>4</sup>, integer multiplication<sup>2,6</sup> and matrix multiplication and some related problems<sup>7</sup>, sorting<sup>8</sup> transitive function<sup>5</sup> and a number of predicates<sup>3,8,9,10</sup>.

In this paper, the problem of merging two sorted arrays is considered. Following the VLSI models discussed in literature<sup>1,2,4,11</sup>. We derive the lower bound for the area-time tradeoffs for this problem. Let  $A$  and  $T$  denote the chip area and computation time required to merge two sorted arrays of length  $N$ , we will show that  $AT^2 = \Omega(N^2 \log^2 N)$  and  $AT^{2x} = \Omega(N^{1+x} \log^{2x} N)$ , for  $0 \leq x \leq 1$ .

### The Merging Problem and VLSI Model

Let  $D = \{0, 1, \dots, K-1\}$  be a set of  $K$  elements. Each element in  $D$  is called a word and can be represented with  $\lceil \log K \rceil$  bits. Let  $D_N = \{(x_1, x_2, \dots, x_N) \mid x_1 \leq \dots \leq x_N, x_i \in D\}$  be the set containing all the sorted arrays of length  $N$ . Let  $\|A\|$  denote the number of elements contained in a set  $A$ , then it is well known combinatorial result that

$$\|D_N\| = \binom{K+N-1}{N} \quad (1)$$

The merging problem can be characterized by the function  $F : D_N \times D_N \rightarrow D_{2N}$ , such that  $F(x_1, \dots, x_N, y_1, \dots, y_N) = (z_1, \dots, z_{2N})$ , where  $X = (x_1, \dots, x_N)$ ,  $Y = (y_1, \dots, y_N)$ ,  $D_N$ ,  $Z = (z_1, \dots, z_{2N}) \in D_{2N}$ , and  $\{x_1, \dots, x_N\} \cup \{y_1, \dots, y_N\} = \{z_1, \dots, z_{2N}\}$ . Arrays  $X$  and  $Y$  are the two input arrays to be merged, and array  $Z$  is the sorted array resulting from the merge.

The VLSI model used in this paper is adopted from those proposed in literature<sup>1,2,4</sup>. A VLSI circuit in our model can be viewed as the layout of a graph in which nodes correspond to logical gates and edges correspond to wires. While the nodes serve as either processing elements or I/O ports, the wires are used for interconnection between gates. We assume that chip layout of a VLSI circuit is a convex planar region. A wire in layout has minimal width  $\lambda > 0$  and can transmit 1 bit of information. It is assumed that at most  $v \geq 2$  wires can overlap at any point in the layout of a VLSI circuit, i.e., there are at most  $v$  layers in a chip. Each node can store a bit and occupies at least  $\rho \geq \lambda^2$  area. As for the processing time, it is assumed that a minimal delay  $\tau$  is required to transmit one bit through a node; this includes the delay over the wires. We also assume that each input is read exactly once and read in form a distinct input port, and that the times and locations at which the inputs are supplied and output are delivered are fixed and independent of the input values. The above assumptions reflect the state of nMOS circuit design methodology and fabrication technology<sup>1</sup>. Details on these assumptions can be found in literature<sup>1,2,11</sup>.

### Lower Bounds

Based on the VLSI model described in the previous section, we will derive in this section a lower bound for  $AT^2$ , where  $A$  and  $T$  are the chip area and computation time of a VLSI circuit that merges two sorted arrays.

Our approach is now a classical one and consists of partitioning the circuit into two regions with roughly equal sizes, and then derive the minimal amount of information necessary to flow between the two sides of the partition during the course of computation. This technique was originally developed in literature<sup>4</sup> and was used to obtain the area time complexity of various problems in literature<sup>2,4-8</sup>. Consider a function  $F(x_1, \dots, x_N) = (z_1, \dots, z_m)$  and a VLSI circuit implementing  $F$ . Let  $L$  and  $R$  be the two regions obtained by partitioning the circuit with a chord perpendicular to the diameter of the layout. We will denote this partition by  $(L, R)$ . Since it is always possible to slide the chord appropriately such that the number of input variables in  $R$  is equal to  $s = \lfloor N/2 \rfloor$ , we will assume throughout this paper that this is true for any partition  $(L, R)$ . Also, for the sake of clarity in the remainder of this section, we assume that each input variable has all its bits input on the same side of partition. To be general we would have to define that a variable is input on the side of the partition where the majority of its bits are input. Since we would still consider at least half of the total number of bits, this would only change our result by a factor of 2.

Let  $X_R = (x_{i1}, \dots, x_{is})$   $i_1 \leq \dots \leq i_s$ , be the variables of  $X$  in  $R$  and  $Z_R = (z_{j1}, \dots, z_{jr})$ , be the variables of  $Z$  in  $R$ , then the information flow from  $L$  to  $R$  is defined in the following definition.

*Definition 1 :* Let

$$F_{X_R \rightarrow C}^{Z_R} = (Z_{j1}, \dots, Z_{jr})|_{x_{i1} = c_1, \dots, x_{is} = c_s},$$

where  $C(c_1, \dots, c_s) \in D_s$  be the restriction of  $F$  to  $Z_R$  obtained by setting the input variables  $x_{i1}, \dots, x_{is}$  to the constants  $c_1, \dots, c_s$  respectively. The information -flow from  $L$  to  $R$  is defined by :

$$I(F) = \phi_{L \rightarrow R} + \phi_{R \rightarrow L}.$$

*Definition 2 :* The cross-flow  $I(F)$  that measures the amount of information that must flow between  $L$  and  $R$  during the computation of  $F$  is defined by

$$\phi_{L \rightarrow R} = \left\lceil \log \max_{C \in D_s} \left\| F \begin{matrix} Z_R \\ X_R \end{matrix} = C \right\| \right\rceil \quad (2)$$

The information-flow from  $R$  to  $L$ ,  $\phi_{R \rightarrow L}$  is defined similarly.

The cross flow  $I(F)$  is related to  $AT^2$  by the following lemma originally due to Thompson<sup>4</sup>.

*Lemma 1* : The are  $A$  and the computation time  $T$  of a VLSI layout satisfy :

$$AT^2 \geq \frac{1}{2} \left( \frac{\lambda \tau}{v} \right)^2 I^2(F), \quad (3)$$

where  $\lambda$ ,  $\tau$  and  $v$  are the parameters discussed in the previous section.

Lets consider now the problem of merging two sorted arrays. Let  $F(x_1, \dots, x_N, y_1, \dots,$

$y_N) = (z_1, \dots, z_{2N})$  be the function that implements merging. For  $1 \leq m \leq N-1$  by choosing  $y_1 = y_2 = \dots = y_m = 0$  and  $y_{m+1} = \dots = y_N = K-1$ , the restriction of  $F$ ,

$$F_m := F: (x_1, \dots, x_N, 0, \dots, 0, K-1, \dots, K-1) \rightarrow (0, \dots, 0, x_1, \dots, x_N, K-1, \dots, K-1), \quad (4)$$

is the function that shifts each input  $x_j$  by  $m$  position. Note that there are  $m$  0's and  $N-m(K-1)$ 's in both parenthesis. Moreover, the sub function  $id: (x_1, \dots, x_N) \rightarrow (z_{m+1}, \dots, z_{m+N})$  is the identify function in that  $z_{m+1} = x_j$ . The function  $F_0$  and  $F_N$  are defined similarly by setting all the  $y_j$ 's to  $(K-1)$  and 0 respectively. The cross flow of  $id$  is derived in lemma 2. The following notation is useful in our derivations: Given a set of subscripted variables  $U \{u_{i1}, \dots, u_{ip}\}$  we let  $S(U)$  denote the set of subscripts  $\{i_1, \dots, i_p\}$ .

*Lemma 2* : Let  $(L, R)$  be a portion of the circuit that implements the identify function  $id(x_1, \dots, x_N) = (z_1, \dots, z_N)$ , where  $X = (x_1, \dots, x_N)$ ,  $Z = (z_1, \dots, z_N) \in D_{Ns}$  and  $z_i = x_j$ ; for  $i \leq j \leq N$ . Let  $X_L$  and  $X_R$  ( $X_L \cup X_R = X$ ) denote the sets of variables of  $X$  that are in  $L$  and  $R$  respectively. Similarly, let  $Z_L$  and  $Z_R$  and  $(Z_L \cup Z_R = Z)$  denote the sets of variables of  $Z$  that are in  $L$  and  $R$  respectively. Let  $\|S(X_L) \cap S(Z_R)\| + \|S(X_R) \cap S(Z_L)\|$ , the cross-flow of  $id$  satisfies.

$$I(id) = \Omega(k \log k), \quad (5)$$

If  $K = N^{1+\varepsilon}$  for some fixed value  $\varepsilon > 0$ .

*Proof :* Assume  $S(X_L) \cap S(X_R) = \{i_1, \dots, i_p\}$  where  $i_1 \leq \dots \leq i_p$ . By grouping all the variables with consecutive indices together, the set  $\{x_{i_1}, \dots, x_{i_p}\}$  can be partitioned into  $t$  disjoint sets :

$$\{x_{i_1}, \dots, x_{i_p}\} = \{x_{i_1}, \dots, x_{i_{p_1}}\} \cup \{x_{i_{p_1+1}}, \dots, x_{i_{p_1+p_2}}\} \cup \dots \cup \{x_{i_{p_1+\dots+p_{t-1}+1}}, \dots, x_{i_{p_1+\dots+p_t}}\},$$

where  $p_j$  is the number of the variables in the  $j^{th}$  group. Note that  $p_1 + \dots + p_t = p$  and  $i_{p_1} = i_1 + p_1 - 1$ ,  $i_{p_1+p_2} = i_{p_1+1} + p_2 - 1$ , ..., etc.

Now lets consider  $\phi_{L \rightarrow R}$ . By choosing proper constant values for the input variables whose indices are not in  $\{i_1, \dots, i_p\}$ , we can derive the lower bound for  $\phi_{L \rightarrow R}$  by counting the number of joints in the range of

$$\left( z_{i_1}, \dots, z_{i_p} \right) \Big| x_j = c_j, j \notin \{i_1, \dots, i_p\},$$

since by the definition of  $\phi_{L \rightarrow R}$ ,

$$\phi_{L \rightarrow R} \geq \log \left\| \left( z_{i_1}, \dots, z_{i_p} \right) \Big| x_j = c_j, j \notin \{i_1, \dots, i_p\} \right\|$$

The constant value  $c_j$  assigned to  $x_j, j \notin \{i_1, \dots, i_p\}$  is defined as follows :

- (i)  $c_j = 0$ , if  $j \leq i_1$ ,
- (ii)  $c_j = a_n$ , if  $j \leq i_1$ , if  $i_{p_1+1} + p_n < j < i_{p_1+1} + p_{n+1}$ , for  $1 \leq n \leq t-1$ ,
- (iii)  $c_j = a_t$ , if  $j > i_{p_1+\dots+p_t}$ ,

where

$$a_n = \sum_{1 \leq i \leq n} (K_i - 1) \text{ and } K_i = \lceil (K-1) p_i/p \rceil \geq 1.$$

Note that the choice of the sequence  $\{a_n\}$  is legal, since  $\{a_n\}$  is increasing and

$$a_t \sum_{1 \leq i \leq t} (K_i - 1) \leq \sum_{1 \leq i \leq t} (K - 1) \frac{p_i}{p} = K - 1.$$

with  $x_j, j \notin \{i_1, \dots, i_p\}$  being fixed to constant values as above, the cardinality of the range of  $(z_{i_1}, \dots, z_{i_p}) \mid x_j = c_j, j \notin \{i_1, \dots, i_p\}$  is equal to the number of solution to the following inequality :

$$0 \leq x_{i_1} \leq \dots \leq x_{i_{p_1}} \leq a_1 \leq x_{i_{p_1+1}} \leq \dots \leq x_{i_{p_1+p_2}} \leq a_2 \leq \dots \leq a_{t-1} \leq x_{i_{p_1+\dots+p_{t-1}+1}} \leq \dots \leq x_{i_{p_1+\dots+p_t}} \leq a_t, \quad (6)$$

And the log of the number of solutions is a lower bound for  $\phi_{L \rightarrow R}$ .

From the fact that the inequality

$$0 \leq x_i \leq \dots \leq x_p \leq K-1 \text{ has } \binom{k+p-1}{p}$$

solution, the total number of solutions to (9) is

$$\binom{K_1 + p_1 - 1}{p_1} \binom{K_2 + p_2 - 1}{p_2} \dots \binom{K_t + p_t - 1}{p_t}$$

thus we have

$$\phi_{L \rightarrow R} \geq \log \prod_{1 \leq j \leq t} \binom{K_j + p_j - 1}{p_j}$$

$$\begin{aligned}
 &= \sum_{1 \leq j \leq t} \log \frac{(K_j + p_j - 1) \dots K_j}{p_j \dots 1} \\
 &\geq \sum_{1 \leq j \leq t} \log \left( \frac{K_j}{p_j} \right)^{p_j} \\
 &\geq \sum_{1 \leq j \leq t} p_j \log \frac{K-1}{p} \\
 &= p \log \frac{K-1}{p} \\
 &= \Omega(p \log p).
 \end{aligned}$$

The last equality follows from the fact that  $p < N$  and the assumption that  $K = N^{1+\varepsilon}$  for some fixed value  $\varepsilon > 0$ .

Similarly if  $\|S(X_R) \cap S(Z_L)\| = q$  ( $q = k - p$ ), then we can show

$$\phi_{R \rightarrow L} = \Omega(q \log q). \quad (7)$$

Since  $f(x) = x \log x$  is a convex function, we have

$$\frac{p \log p + q \log q}{2} \geq \frac{p+q}{2} \log \frac{p+q}{2} \quad (8)$$

$$\text{This gives } I(id) = \Omega(k \log k). \quad (9)$$

Consider now the merge problem. Let  $(L, R)$  be a partition of the circuit that implements  $F(X, Y) = (Z)$  where  $X, Y \in D_N$  and  $Z \in D_{2N}$ . We will introduced some useful notations as follows. Let  $F_m$  be the function that shifts each input variable  $x_j$  by  $m$  positions as defined in (6), and  $X_L, X_R, Z_L$  and  $Z_R$  be defined the same as in lemma 2. If  $\{x_i\}$   $i \in I$  is a set of subscripted variables, then define  $X^m = \{X_{i+m}\}$   $i \in I$ . Let  $\Psi(F_m)$  be defined by

$$\Psi(F_m) = \|S(X_L^m) \cap S(Z_R)\| + \|S(X_R^m) \cap S(Z_L)\|. \quad (10)$$

Note that  $\Psi(F_m)$  measures the number of variables that "cross" through the partition of the circuit, i.e. the number of variables whose input ports and output ports lie in different sides of the partition.

The following lemma shows that there exists at least an  $m$ ,  $1 \leq m \leq N$ , for which the number of variables crossing the partition is  $\Omega(N)$ .

*Lemma 3* : There exists at least an  $m$ ,  $1 \leq m \leq N$ , such that  $\Psi(F_m) \geq \lfloor N/8 \rfloor$ .

*Proof*: Let's consider the  $\lceil N/2 \rceil$  output variables  $x_{\lfloor N/2 \rfloor + 1}, \dots, x_N$  and the  $\lceil N/2 \rceil$  output variables  $z_{N+1}, \dots, z_{N+\lceil N/2 \rceil}$ .

Only for each such  $z_j$  and  $x_i$ ,  $x_j$  is mapped to  $z_j$  by  $F_m$  where  $1 \leq m = j-1 \leq N$ . Therefore, by counting through all the  $F_m$ ,  $1 \leq m \leq N$ , we have

$$\sum_{1 \leq m \leq N} \Psi(F_m) \geq (\lceil N/2 \rceil) \min(l, r), \quad (11)$$

$$\sum_{1 \leq m \leq N} \Psi(F_m) \geq (\lceil N/2 \rceil) \lceil N/2 \rceil / 2 \quad (12)$$

and there must exist an  $m$ ,  $1 \leq m \leq N$ , such that  $\Psi(F_m) \geq \lfloor N/8 \rfloor$ .

where  $l$  and  $r$  are the number of input variables  $x_i$ ,  $\lfloor N/2 \rfloor + 1 \leq i \leq N$ , which are in  $L$  and  $R$  respectively. Since  $\lfloor N/2 \rfloor \leq l$ ,  $r \leq \lceil N/2 \rceil$ , we have

$\sum \Psi(F_m) \geq 1 \leq m \leq N \lfloor N/2 \rfloor \lfloor N/2 \rfloor / 2$ , and there must exist an  $m$ ,  $1 \leq m \leq N$  such that  $\Psi(F_m) \geq \lfloor N/8 \rfloor$

Combining lemma 2 and lemma 3, it follows that

$$I(F_m) = \Omega(N \log N). \quad (13)$$

*Theorem* : If  $A$  is the chip area and  $T$  is the computation time required to merge two sorted arrays of lengths  $N$ , then

$$AT^2 = \Omega(N^2 \log N) \text{ and} \quad (14)$$

$$AT^{2x} = \Omega(N^{1+x} \log^{2x} N), \quad (15)$$

for  $0 \leq x \leq 1$ , if  $K = N^{1+\varepsilon}$  for a fixed value  $\varepsilon > 0$ .

*Proof:* Since  $F$  can realize each  $F_m, 1 \leq m \leq N$ , equation (14) follows directly from lemma 1 and equation (15).

As for equation (15), consider the time when all the  $\lceil N/2 \rceil$  input variables  $x_{\lceil N/2 \rceil+1}, \dots, x_N$  have been read. None of the  $\lceil N/2 \rceil$  variables  $z_{N+1}, \dots, z_{N+\lceil N/2 \rceil}$  have been output, since each  $x_i$  can be routed to each  $z_j$  by some  $F_m$ . These  $\lceil N/2 \rceil$  output variables can assume  $2^{\lceil N/2 \rceil}$  distinct values; the circuit is therefore required to memorize  $\lceil N/2 \rceil$  bits of information in order to assume  $2^{\lceil N/2 \rceil}$  internal states. From the assumption in section 2 that each node occupies at least  $\rho$  area, we conclude that

$$A \geq \rho \lceil N/2 \rceil. \quad (16)$$

Equation (15) then follows directly from equation (14) and (16).

### Conclusion

Following the VLSI model described in section 2, we have derived in the previous section lower bounds for the area-time tradeoffs for the merging two sorted arrays of lengths  $N$  is  $AT^{2x} = \Omega(N^{1+x} \log^{2x} N)$ , For  $0 \leq x \leq 1$ ,  $K = N^{1+\varepsilon}$  for a fixed value  $\varepsilon > 0$ . This shows that the inherent computational complexities for sorting and merging are asymptotically identical in the VLSI model<sup>12</sup> unlike in the conventional model of sequential computation.

Although we required, in the proof given in the paper, that such input appear on a distinct input port, this assumption can easily be relaxed and it can be assumed that I/O ports are multiplexed. The proof would then follow arguments similar to the ones given in<sup>12</sup> for examples.

Consider the general case of the merging problem in which the lengths of the two arrays to be sorted may not be the same. Lets assume that the lengths of these two arrays be  $M$  and  $N$ , where  $M \geq N$ . From our results, it can be shown that the lower bound on area-time complexity for this general problem is  $AT^{2x} = \Omega(N^{1+x} \log^{2x} N)$  for  $0 \leq x \leq 1$ . This lower bound is however not tight for the case when  $M$  is very large, compared with  $N$ . A typical example of this is the case when  $N=1$ . In that case, the merging problem is equivalent to the problem of inserting an element into a sorted arrays. An interesting open problem is therefore to obtain better lower bound for this general case of merging problem.

### References

- 1 Mead, C A & Conway, L A (1980) *Introduction to VLSI Systems*, Addison -Wesley, Reading, Massachusetts
- 2 Brent, R P & Kung H T (1993) *Jour of the ACM* **28(3)** · 521
- 3 Lipton, R.J & Sedgewiek, R (1991) *Proceedings of the 13<sup>th</sup> Annual ACM Symposium on Theory of Computing*, p 300
- 4 Thompson, C D (1979) *Proceedings of the 11<sup>th</sup> Annual ACM Symposium on Theory of Computing*, p 81
- 5 Vuillemin, J (1983) *IEEE Transaction on Computers* **C-32(3)** . 294.
- 6 H Abeslon, H & Andreae, P (1990) *Communications of the ACM* **23(1)** 20
- 7 Savage, J E (1981) *Jour of Computer and System Sciences* **22(2)** 230
- 8 Brent, R P & Goldschlager, L M (1998) *SIAM Jour on Computing* **11(4)** 737
- 9 Savege, J E (1991) *Planar Circuit Complexity and the performance of VLSI Algorithm in VLSI Systems and Computations*, H T Kung, B. Sproull & G Steele (eds ), Computer Science Press, p. 61
10. Yao A C. (1981) "*The Entropic Limitations on VLSI Computations* " *Proceedings of the 13<sup>th</sup> Annual ACM Symposium on Theory of Computing*, p 308
- 11 Baudet, G M. (1993) *Algorithms and Complexity* **49** · 74
- 12 Mishra, P K. & Sharma, C.K. (2001) *Proc Nat Acad. Sci. India* **71(A)III** · 213.

## Equilibrium studies on mixed ligand complexes— Evidence of stacking interactions-solution studies

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### Abstract

Interaction of bivalent metals with maltol or kojic acid and selected amino acids (Alanine,  $\beta$ -phenylalanine, L-tyrosine, L-DOPA and tryptophan) has been investigated by potentiometric pH measurements at 30 °C and  $\mu = 0.1 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ). The stability order of these ternary complexes is in the order Ph alanine < tyrosine < DOPA < Tryptophan. The extra stabilisation and above sequence of order is attributed to stacking interactions in ternary complexes.

(**Keywords:** potentiometry / ternary complexes / formation constants / maltol / kojic acid / amino acids).

In continuation to our earlier work<sup>1-3</sup> on ternary metal complexes of  $\gamma$ -pyrones, we now report the formation constants of ternary complexes of type MAL [where M = Co(II), Ni(II), Cu(II) and Zn(II); L = 3-hydroxy-2-methyl-pyran-4-one (maltol) or 5-hydroxy-2(hydroxymethyl)pyran-4-one (kojic acid); A = amino acids (*viz.* alanine, phenyl alanine, tyrosine, tryptophan and 3, 4 dihydroxyphenyl alanine (DOPA)] which have been determined potentiometrically at 30°C and  $\mu = 0.1 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ) in aqueous medium.

The ligands, maltol and kojic acid are obtained from Lancaster (U.K.). The amino acids are obtained from Sigma Chemical Company. The metal salts of Co(II), Ni(II), Cu(II), and Zn(II) are of AnalaR grade and their solutions are standardized volumetrically by titration with the sodium salt of EDTA.<sup>4</sup> Potentiometric measurements are carried out at 30°C in aqueous medium (with 0.1 M  $\text{KNO}_3$  as background electrolyte) using control dynamics pH meter. The pH meter readings are plotted against  $a$  (moles of base added per mole of ligand) or  $m$  (moles of base added per mole of metal ion). Calculations were carried out with the help of computer program - BEST.<sup>5</sup> The calculated ternary stability constants are reported in Table 1. Table 2 lists the  $\Delta \log K$  values along with  $\Delta \Delta \log K$  values. The parameters,  $\Delta \log K$  and  $\Delta \Delta \log K$  are used to characterize the stability of ternary complexes formed. The extra stability found in ternary complexes is due to stacking interactions.

The stacking interactions, can be quantised with suitable parameters associated with the following equilibrium:

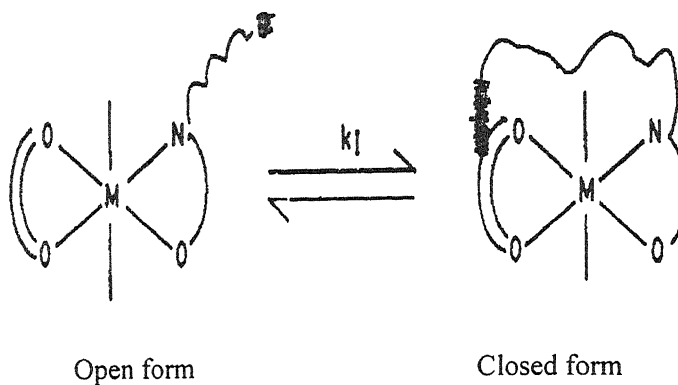


Table 1- Logarithms of stability constants ( $\log K_{MLA}^M$ ) of ternary complexes  
 $[T = 30^\circ\text{C}, \mu = 0.1 \text{ mol dm}^{-3} (\text{KNO}_3), \text{aqueous medium}]$

| Secondary Ligands (A)            | Co(II) | Ni(II) | Cu(II) | Zn(II) |
|----------------------------------|--------|--------|--------|--------|
| Kojic acid as primary ligand (L) |        |        |        |        |
| alanine                          | 8.65   | 10.06  | 14.05  | 9.56   |
| Ph.alanine                       | 8.53   | 9.78   | 13.78  | 9.21   |
| Tyrosine                         | 8.02   | 9.43   | 13.15  | 9.08   |
| DOPA                             | 8.65   | 9.97   | 14.16  | 9.23   |
| Tryptophan                       | 8.70   | 9.99   | 13.90  | 9.58   |
| Maltol as primary ligand (L)     |        |        |        |        |
| alanine                          | 9.28   | 10.77  | 15.14  | 10.26  |
| Ph.alanine                       | 9.20   | 10.55  | 14.91  | 9.99   |
| Tyrosine                         | 8.70   | 10.20  | 14.26  | 9.83   |
| DOPA                             | 9.34   | 10.75  | 15.31  | 10.01  |
| Tryptophan                       | 9.35   | 10.71  | 15.04  | 10.32  |

Sigma fit values are in the range  $\pm 0.05$  to  $0.08$  log units

The concentration independent and dimensionless constant  $K_1$  for intramolecular equilibrium is calculated by the relationship:

$$K_1 = 10^{\Delta \log K - 1} \quad (1)$$

The parameter  $\Delta \log K$  is given by relationship

$$\Delta \log K = (\log K_1 - \log K_2) \quad (2)$$

where  $\log K_2$  is for the reaction  $[M^{2+} + L + Ala]$  and  $\log K_1$  relates to the reaction  $[M^{2+} + L + \text{other amino acids}]$ . The values thus obtained are given in Table 2.

Table 2—Comparison of  $\log K$  and  $\Delta \log K$  values for ternary complexes

$[T = 30^\circ\text{C}, \mu = 0.1 \text{ mol dm}^{-3} (\text{KNO}_3), \text{aqueous medium}]$

| Secondary Ligands (A)            | Co(II)  | Ni(II)  | Cu(II)  | Zn(II)  |
|----------------------------------|---------|---------|---------|---------|
| Kojic acid as primary ligand (L) |         |         |         |         |
| alanine                          | -0.38   | -0.37   | -0.45   | -0.39   |
| Ph alanine                       | -0.32   | -0.27   | -0.31   | -0.33   |
|                                  | (+0.06) | (+0.10) | (+0.14) | (+0.06) |
| Tyrosine                         | -0.29   | -0.25   | -0.26   | -0.26   |
|                                  | (+0.09) | (+0.12) | (+0.19) | (+0.13) |
| DOPA                             | -0.26   | -0.16   | -0.21   | -0.26   |
|                                  | (+0.12) | (+0.21) | (+0.24) | (+0.13) |

Table 2 Contd

Table 2 Contd

|                              |                  |                  |                  |                  |
|------------------------------|------------------|------------------|------------------|------------------|
| Tryptophan                   | -0.20<br>(+0.18) | -0.12<br>(+0.25) | -0.15<br>(+0.30) | -0.18<br>(+0.21) |
| Maltol as primary ligand (L) |                  |                  |                  |                  |
| alanine                      | -0.35            | -0.30            | -0.40            | -0.32            |
| Ph alanine                   | -0.25<br>(+0.10) | -0.14<br>(+0.16) | -0.22<br>(+0.18) | -0.18<br>(+0.14) |
| Tyrosine                     | -0.21<br>(+0.14) | -0.12<br>(+0.18) | -0.19<br>(+0.21) | -0.14<br>(+0.18) |
| DOPA                         | -0.17<br>(+0.18) | -0.02<br>(+0.28) | -0.10<br>(+0.30) | -0.11<br>(+0.21) |
| Tryptophan                   | -0.15<br>(+0.20) | -0.04<br>(+0.26) | -0.05<br>(+0.35) | -0.07<br>(+0.25) |

$\Delta \log K = [\log K_{MLA}^M - \log K_{MA}^M + \log K_{ML}^M]$ . The  $\Delta \log K$  values are presented in paranthesis.

$\Delta \log K = [\Delta \log K_1 - \Delta \log K_2]$ , where  $\Delta \log K_1$  is for the reaction (M + L + amino acids except alanine) and  $\Delta \log K_2$  is for the reaction (M + L + alanine).

Alanine is taken as a reference for zero based stacking interactions

The percentage of stacked isomers in the systems is also calculated with the relationship:

$$\%(MLA)_{St} = [100 * K_1 / (1 + K_1)] \quad (3)$$

The values of  $K_1$  and  $\%(MLA)_{St}$  for these systems are presented in Table 3. The perusal of parameters associated with stacking interactions reveal the following observations :

Table 3—Parameter showing the extent of intramolecular stacking interaction in ternary complexes  
 $[T = 30^{\circ}\text{C}, \mu = 0.1 \text{ mol dm}^{-3} (\text{KNO}_3), \text{aqueous medium}]$

| Secondary Ligands (A)                | Parameters | Co(II) | Ni(II) | Cu(II) | Zn(II) |
|--------------------------------------|------------|--------|--------|--------|--------|
| Kojic acid as primary ligand (L)     |            |        |        |        |        |
| Ph alanine                           | $K_1$      | 0.148  | 0.258  | 0.380  | 0.148  |
|                                      | % (MLA)st  | 12.89  | 20.50  | 27.54  | 12.89  |
| Tyrosine                             | $K_1$      | 0.230  | 0.3182 | 0.548  | 0.348  |
|                                      | % (MLA)st  | 18.70  | 24.13  | 35.44  | 25.82  |
| DOPA                                 | $K_1$      | 0.318  | 0.622  | 0.738  | 0.479  |
|                                      | % (MLA)st  | 24.13  | 38.35  | 42.46  | 32.38  |
| Tryptophan                           | $K_1$      | 0.513  | 0.778  | 0.995  | 0.622  |
|                                      | % (MLA)st  | 33.91  | 43.75  | 49.88  | 38.35  |
| Maltol as primary ligand (L)         |            |        |        |        |        |
| Ph alanine                           | $K_1$      | 0.258  | 0.445  | 0.513  | 0.380  |
|                                      | % (MLA)st  | 20.50  | 30.79  | 33.91  | 27.54  |
| Tyrosine                             | $K_1$      | 0.380  | 0.513  | 0.622  | 0.513  |
|                                      | % (MLA)st  | 27.54  | 33.91  | 38.35  | 33.91  |
| DOPA                                 | $K_1$      | 0.513  | 0.9054 | 0.9952 | 0.622  |
|                                      | % (MLA)st  | 33.91  | 47.51  | 49.88  | 38.5   |
| Tryptophan                           | $K_1$      | 0.585  | 0.8197 | 1.238  | 0.778  |
|                                      | % (MLA)st  | 36.91  | 45.04  | 55.32  | 43.75  |
| *Benzimidazole as primary ligand (L) |            |        |        |        |        |
| Ph alanine                           | $K_1$      | 1.137  | 1.691  | 1.344  | 1.041  |
|                                      | % (MLA)st  | 53.20  | 62.83  | 57.33  | 51.00  |
| Tyrosine                             | $K_1$      | 1.344  | 1.818  | 1.884  | 1.238  |
|                                      | % (MLA)st  | 57.33  | 64.51  | 65.33  | 55.31  |
| DOPA                                 | $K_1$      | 1.187  | 1.691  | 1.454  | 1.089  |
|                                      | % (MLA)st  | 54.27  | 62.83  | 59.25  | 52.13  |
| Tryptophan                           | $K_1$      | 1.454  | 2.235  | 2.235  | 1.630  |
|                                      | % (MLA)st  | 59.25  | 69.08  | 69.08  | 61.97  |

\* Data for benzimidazole is abstracted from the reference. Usha Rani, G & DD Manwal (1998)  
*J. Electrochem Soc India*. 47-4 : 224

- (a) The stacking interactions decrease in the order: tryptophan > tyrosine > DOPA > ph.alanine. This order can be correlated with the size of the aromatic side chain. Stacking in ternary complexes containing tryptophan results in maximum<sup>6</sup> stabilization since the surface area of the indole ring is large and permits for efficient stacking with kojic acid or maltol. The phenyl rings of ph.alanine and tyrosine are small and hence lower efficiency of stacking.

The ligand DOPA is an ambidentate ligand. DOPA can bind to metal ion either like glycine using amino carboxylic group or it can bind like pyrocatechol using both oxygens present on phenyl ring. It is well known that in lower pH, DOPA binds to metal ion through amino carboxylate end and at higher pH it binds like catechol. However as observed by Bhattacharya, the present study also shows that DOPA binds in ternary complexes from the amino carboxylate ends over the pH range of 4-7.

- (b) The % of stacking interaction decreases in the order Cu(II) > Ni(II) > Zn(II) > Co(II) with respect to the metal ions. This order is in confirmity with Irving Williams natural order of stabilities<sup>8</sup>.
- (c) The stability sequence with respect to primary ligand is in the order: Maltol > Kojic acid. This sequence is in line with basicity order. Maltol is more basic than kojic acid hence forms more stable complex.
- (d) The present communication deals with stacking interaction between aromatic moiety of one ligand and  $\pi$  electron cloud of another ligand. Earlier we have published a paper in which two ligands have aromatic moieties (eg. benzimidazoles as primary ligand and amino acids as secondary ligand). We thought it worthwhile to compare the extent of stacking interactions in these two different systems. Hence, we have reproduced the data of benzimidazole in Table 3. Comparison of % of stacked form from table 3 reveals the order : [benz-Cu-tryptophan](69.08%) > [maltol-Cu-tryptophan](55.32%) > [kojic acid-Cu-tryptophan] (49.88%). Complex containing benzimidazole forms much better stacked complex than ternary complex of maltol or kojic acid. The reason is simple, the benzimidazole is aromatic whereas maltol or kojic acid are non-aromatic.

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### References

1. Manwal, Devadas, UshaRani, G & Yogibabu, N (1998) *J Electrochem Soc India* **47**(1) 55
2. Manwal, Devadas & Shankaraiah, D (1998) *J Electrochem Soc India* **47**(1) 59.
3. Manwal, Devadas & Shankariah, D (2000) *Natl Acad Sci Letters* **23**(11&12) 159
4. Schwarzenbach (1957) *Complexometric titration* Interscience, New York p 77
5. Motekaitis, R.J. & Martell, A E. (1982) *Can J Chem* **60** 168 & 2403.
6. Prasad, K & Srinivas Mohan, M (1987) *J Coord Chem* **16** . 1.
7. Patel, V. K. & Battacharya, P K (1984) *J Inorg Biochemistry* **21** 169
8. Irving, H & Williams, R J P (1953) *J Chem Soc* 3192.

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